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SURFACE AREA MEASUREMENT OF SMALL PARTICLES BY LIQUID-PHASE ADSORPTION OF STEARIC ACID

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Preston Talmage Bankston

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SURFACE-AREA MEASUREMENT OF SMALL PARTICLES BY

LIQUID-PHASE ADSORPTION OF STEARIC ACID

Approved:

Thesis Adviser

Date Approved by Chairman: Oct. 13, 1953

PREFACE

I wish to pay tribute to my wife, Verleen Beryl Bankston, whose patience, understanding, and assistance made this work possible.

To Dr. J. M. DallaValle I am deeply indebted for suggesting the thesis problem and for his invaluable guidance and assistance during the course of the investigation. I wish to express my appreciation to Dr. R. F. Sessions, whose discussions clarified many aspects of the problem; to Mr. Glenn Blocker, who made the BET surface area measurements; and to Drs. F. Bellinger and H. V. Grubb, who read the text and made many helpful suggestions. I am very grateful also to the Research Corporation for sponsoring the fellowship which made this work possible.

P. Talmage Bankston

Atlanta, Georgia
October, 1953

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ABSTRACT

The industrial use of finely divided solids has increased many-fold during the past few years. In such fields as powder metallurgy, ceramics, catalysis, separation of isomers, and concentration of rare earths, small particles are used extensively. One out-growth of this wide-spread utilization of fine powders has been an increased interest in the study of the surface properties of finely divided material.

The measurement of the surface area of a solid is obviously of fundamental importance to a study of its properties. Generally, the methods available for the evaluation of surface area fall into one of two categories: (1) direct methods wherein some measure of particle diameter is obtained or (2) indirect methods in which use is made of certain physico-chemical properties of the surface.

While a useful and somewhat comparable measure of particle size is obtained by use of the direct methods (e.g., microscopic examination, sieve analysis), surface area values so obtained are generally unreliable. This is due to lack of knowledge regarding particle shape and structure; consequently the relation between particle size and surface area is unknown. These methods are further limited in that pores and fissures escape detection in most instances.

The indirect methods, of which permeometric measurements, heat-of-wetting measurements, sedimentation techniques, and various adsorption techniques are typical, usually are based upon some sort of interaction between the surface atoms of the solid and atoms or molecules

of the surrounding media. Of the indirect methods, the most accurate are those techniques based upon adsorptive processes of one kind or another.

The most widely used of the adsorption techniques is the one developed by Brunauer, et al., commonly known as the BET procedure. While some of the underlying assumptions of the BET theory are erroneous, the surface area values obtained by use of this theory are generally accepted as being quite accurate. This method of surface area determination, however, has not been utilized to its fullest extent, since it requires rather elaborate equipment and an excessive amount of time.

The objective of this investigation was to evaluate the use of the adsorption of stearic acid from solution as a rapid means of measuring the surface area of particulate matter; to evolve, if possible, improvements to present techniques used for this purpose; and to delineate the limitations of present techniques.

In the adsorption of stearic acid from solution each adsorbed molecule is assumed to be oriented with its longest axis normal to the surface of the solid, with the polar, carboxylic group attached to the solid surface. There is good evidence in the literature that this is the orientation of the adsorbed molecules. Furthermore, the area occupied by each adsorbed molecule is assumed to be the same as that of a molecule in a close-packed film on water. The generally accepted value of 20.5 Å^2 per molecule was used throughout this study.

The adsorption of stearic acid was measured from solutions of benzene, hexane, methanol, and cyclohexane onto the solids nickel,

iron, clay, and titanium dioxide over a rather wide concentration range. When the amount of acid adsorbed was plotted as a function of the relative concentration (i.e., the ratio of the equilibrium concentration to the saturation concentration), it was found that the amount adsorbed by the materials studied in all cases reached a maximum at fairly low values of relative concentration and remained constant thereafter. Data of other workers plotted in this same manner gave similar results. This would indicate that to determine the surface area--assuming that the maximum amount adsorbed corresponds to a unimolecular layer--it is necessary to make only one measurement, if this is made at a relative concentration high enough so that this point is on the flat portion of the isotherm. A number of single-point determinations seem to confirm this observation.

In gas-phase studies, degassing of the sample is essential if reproducible and accurate results are to be obtained. It has been reported that for non-porous alumina and for metals and metal oxides, the extent of adsorption was essentially the same whether the samples were degassed or not. Presumably the organic solvent will displace loosely held, adsorbed gases. This was found to be true to a large extent for a number of kaolins and titanium dioxide as well as metals and metal compounds, although in some instances degassing of these materials was necessary before results in agreement with BET values could be obtained.

The amount of stearic acid in solution after adsorption was determined by conductometric titration or by use of a Langmuir trough in a comparative method of analysis which was found to be both accurate

and rapid.

The values obtained for the surface area of solids as determined from measurement of the adsorption of stearic acid from solution are generally in good agreement with the results obtained by the BET method. While surface area values determined by stearic acid adsorption are not as accurate as those determined by the BET procedure, this technique has the advantage of requiring less elaborate equipment and, for those cases in which degassing is not required, of taking much less time.

The accuracy of surface area values obtained by the adsorption of stearic acid from solution can be ascertained only by comparison with some other standard (the BET values in this study). The technique should be of value, nevertheless, particularly in those cases in which it is necessary to know only the relative value of the surface area of a powder compared to another powder of the same substance.

CHAPTER I

INTRODUCTION

In recent years a considerable amount of interest has been directed toward the study of the surface properties of finely divided materials. The measurement of the surface area of a solid is obviously of fundamental importance to a study of its properties.

There are a number of methods available for the determination of the surface area of particulate matter. They fall into one of two classifications--direct methods of particle-size measurement, exemplified by microscopic examination and sieve analysis; or indirect methods, which make use of certain physico-chemical properties exhibited by the surface.

The direct methods may be used if the particles are confined to narrow limits of size (6). From these methods the average particle "diameter" and the distribution of particle "diameters" may be obtained. However, for these values to be used in calculation of the surface area of the material, it is necessary to make assumptions as to the average geometric shape of the particle. These methods are further limited in that crevices and pores escape detection. Furthermore, apparent particles may in reality be agglomerates. Such an instance is shown in Figures 1 and 2.

The indirect methods comprise the more widely used techniques such as permeometric measurements, heat-of-wetting measurements, sedimentation techniques, and various techniques depending upon adsorptive processes.

The sedimentation and permeometric procedures for surface area measurement do not measure internal surface and are in general limited to particle sizes greater than ten microns. The heat-of-wetting technique due to Harkins and Jura (10) is perhaps the most theoretically sound method in use; however, it is the most difficult and tedious. This method is based on the fact that if a non-porous crystalline solid, whose surface is in equilibrium with the vapor of a liquid, is immersed in the liquid, heat will be evolved due to the loss of the surface energy of the adsorbed film. Each square centimeter of the surface film will give off an amount of heat corresponding to that which would be given off if many small droplets of liquid with a total area of one square centimeter were immersed in a body of the same liquid. Since this quantity can be determined for the liquid from its surface tension and the temperature variation of its surface tension, the area of the solid can be determined if the relationship between the area of the solid and that of the film is known. Normally, the error is small if it is assumed that the two areas are equal.

Of the adsorption methods, the particular one (or modifications thereof) developed by S. Brunauer, P. H. Emmett, L. S. Deming, W. E. Deming, and E. Teller (3,4)--usually referred to as the BET method--is the most widely used. This technique consists, in effect, of measuring the volume of a gas--usually nitrogen--adsorbed at the temperature of the boiling point of the adsorbate. In other gas-phase adsorption procedures, the extent of adsorption is determined gravimetrically (24). A number of liquid-phase adsorption techniques have been reported. Adsorption of various dyes, iodine, and surface-active agents such as the fatty acids have been used.

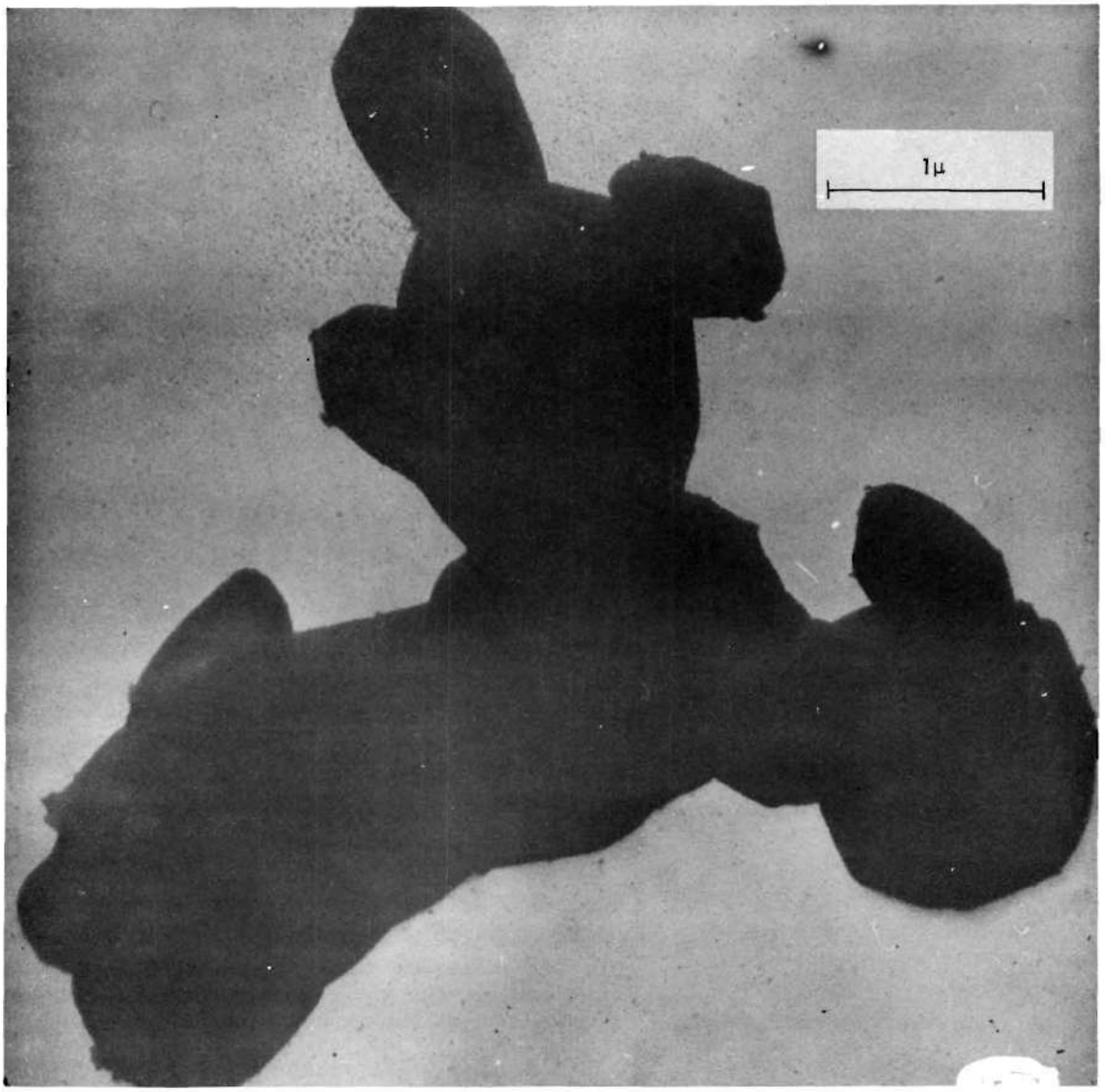

Figure 1. Electron Photomicrograph of Potassium Perchlorate Particle.

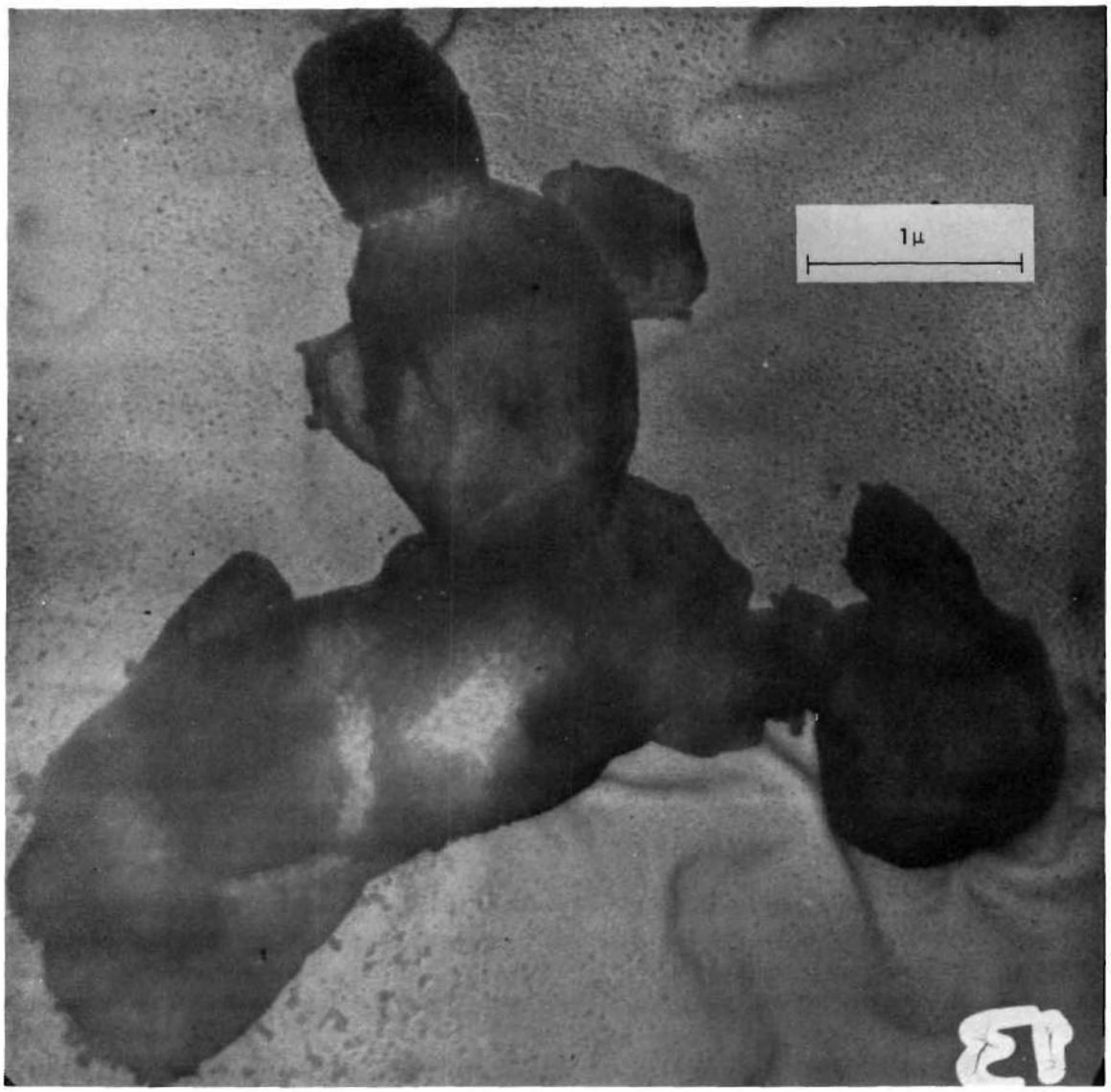

Figure 2. Electron Photomicrograph of Potassium Perchlorate Particle After Exposure to Intensified Electron Beam, Showing Agglomerate Structure.

Of all these methods, the fatty-acid adsorption has the attribute of being comparatively simple and rapid for use as an engineering-control measure. In this method, which consists of adsorption in solution, it is assumed that oriented fatty-acid molecules form a single layer on the material whose surface is to be measured. However, there are many questions in technique to be resolved, and it is the purpose of this thesis to investigate the use of stearic acid as a means of measuring surface area and, if possible, to evolve improvements in present techniques.

CHAPTER II

THEORY OF ADSORPTION

A. Background

When a small quantity of a non-volatile and insoluble substance is placed on the surface of a liquid such as water, which has a high surface tension, the substance may behave in one of two ways: it may remain intact as a solid mass or it may spread over the surface in a thin film. In order for the substance to spread as a film it is a necessary and sufficient condition that the forces of attraction between the water surface and the molecules of the spreading material be greater than the forces between the individual molecules (1). When such is the case, as many of the molecules of the spreading substance as can, move into direct contact with the underlying substance, forming as thin a film as possible. The limiting value that the thinness may attain is obviously a film one molecule thick.

At least one of the properties of surface films of oil on water has been known since antiquity--their power of protecting ships in a rough sea by hindering the breaking of waves. The surface currents set up by substances spreading on water were observed by Benjamin Franklin, who noticed that dead flies soaked in oil moved about vigorously upon a surface of water. In subsequent work with films of oil on water, Lord Rayleigh (31) in England and Miss Pockels (29) in Germany established that the films were, if area permitted, only one molecule thick. Langmuir (19) introduced new experimental methods of great importance which resulted

in new conceptions concerning these films.

Instead of working with oils, Langmuir used pure substances of known constitution and observed the effect of varying this constitution. He measured the outward pressure of the films directly by use of a floating barrier with a device to measure the force on it. The clearest results were obtained with normal, saturated, fatty acids and alcohols. Langmuir found that as the area over which the film was spread was reduced, no appreciable surface pressure developed until the area per molecule had been reduced to approximately 22 $Å^2$, at which point the pressure increased very rapidly with further decreases in area. Figure 3 shows the variation between surface pressure and area per molecule for fatty acids on water. One of the most striking facts illustrated by Langmuir's work is that the area is independent of the length of the chain for chain lengths of 14 to 34 carbon atoms. This would indicate that the molecules are oriented steeply to the surface and are oriented in the same manner in all the films, regardless of chain lengths.

In 1931 Harkins and Gans (9) reported the adsorption of fatty acids from solution as a means for determining the surface area of powders. Since then, several investigators have used this adsorption procedure as a means of estimating the surface area of various metals, metal oxides, and other powders. The surface area values for nickel and platinum catalysts as determined by fatty-acid adsorption by Smith and Fusek (34) were found to give essentially the same results as BET nitrogen-gas adsorption; however, Ries, Johnson, and Melik (32) found only order-of-magnitude agreement between the two methods for the surface

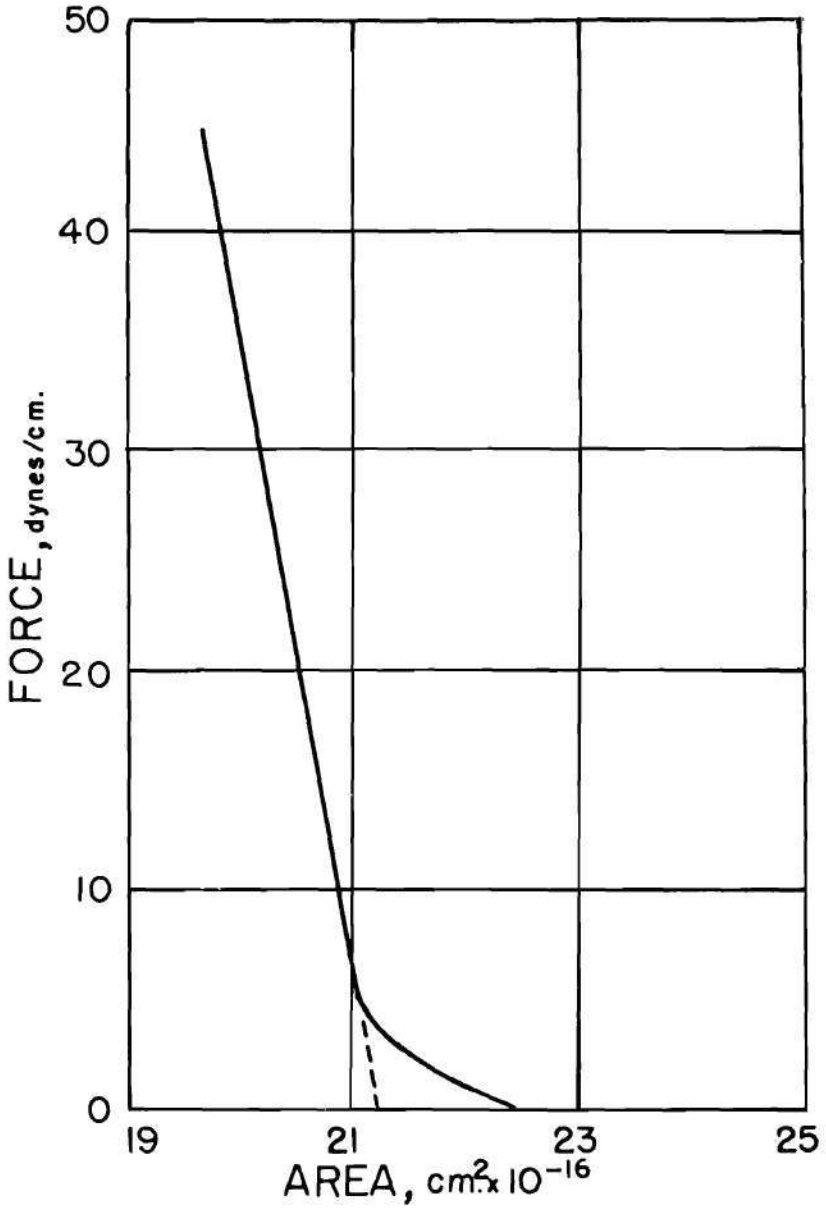

Figure 3. Force-Area Curve for Monomolecular Film of Saturated Fatty Acid on Water at 20° C.*

*Data from Markley (22).

areas of several highly porous, supported catalysts. Work with carbon black by Smith and Hurley (35) and by Linner and Williams (21) indicates that adsorption is affected not only by size and distribution of pores but also by the previous treatment of the carbon surface. Orr and Bankston (27) found good agreement between fatty-acid adsorption and BET results on a number of clays.

Greenhill (8) found that stearic-acid adsorption onto a number of finely divided metals was not appreciably affected by the presence of an oxide film on the powders. The effect which the presence of adsorbed water had on adsorption was found to depend on the powder. For unreactive powders such as TiO_2, SiO_2, TiC, and SiC the presence of water merely reduces the amount of acid adsorbed; whereas for reactive powders such Cu, Cu_2O, CuO, and Zn the presence of water seems to initiate chemical reaction.

B. Theory

1. Orientation and effective area of adsorbed molecules.--It is necessary to know the orientation and effective area covered by the adsorbed molecules in order to evaluate the surface area of a solid from adsorption measurements. With regard to the orientation of the adsorbed molecules, there is good evidence that the molecules arrange themselves perpendicular, or very nearly so, to the surface of the substrate. Langmuir's (19) work showed this type of orientation to occur at liquid surfaces. Mentor and Tabor (26) have shown from electron-diffraction studies of fatty acid and soap films adsorbed on metal surfaces that the molecules are oriented normal to the surface at room temperatures.

As the temperature is raised, a disorientation is observed at some characteristic temperature. This is a true disorientation effect, since as the temperature is lowered orientation is again observed. It was found that on non-reactive metals such as platinum, the disorientation temperature is close to the bulk melting point of the fatty acid. On reactive metals such as zinc and cadmium the disorientation occurs at a higher temperature which is close to the bulk melting temperature of the corresponding metallic soap, thus suggesting that chemical reaction has occurred.

The effective area covered by an adsorbed fatty-acid molecule is generally taken to be the same as that occupied by the molecule in a close-packed film on water. This value for stearic acid has been reported variously as 20.5 (1) to 25.1 (21) Å^2 per molecule. Vold (36) has suggested that, since fatty-acid molecules are elliptical in cross section, the observed molecular cross-sectional area of 25.1 Å^2 corresponds to the area for free rotation; whereas the value of 20.5 Å^2 corresponds to the area for closest packing of ellipses.

That the adsorbed molecule could exhibit several distinct and different areas is not to be disregarded. Harkins and his co-workers (11) have shown that the mean molecular area of nitrogen when adsorbed is not a constant value, but varies with the nature of the substrate. The molecular area of the adsorbed molecules was reported to vary from 13.6 to 16.9 Å^2 per molecule. The distribution of areas was not "normal" but rather tri-modal, with peaks at 14.0, 15.2, and 16.1 Å^2 per molecule, the largest number having the value of 15.2 Å^2. This finding is in support of other knowledge of the effect of substrates on phase changes in monolayers. While this may introduce some uncertainty into the values

for areas of some very polar solids, it does not seriously reduce the utility of adsorption for determining surface area values.

2. Gibbs adsorption equation.--An exact relation between adsorption and surface tension was first derived by J. Willard Gibbs in 1878. The Gibbs adsorption equation may be derived from purely thermodynamic considerations. As this derivation can be found in many textbooks it will not be given here. For a two component system, i.e., one solute and one solvent at constant temperature, Gibbs's relation can be put in the form

$$d\gamma = -\Gamma_2 d\mu_2 \tag{1}$$

where γ is the interfacial tension, i.e., the interfacial energy per sq. cm.; μ_2 is the chemical potential of component 2 (solute); and Γ_2 is the adsorption: the excess of component 2 in some arbitrarily placed "surface of discontinuity" over its concentration in the bulk phase.*

Since

$$\mu_2 = \mu_2^\circ + RT \ell n a_2, \tag{2}$$

equation (1) can be put in the form

$$\Gamma_2 = -\frac{1}{RT}\frac{d\gamma}{d\,\ell n a_2} = -\frac{a_2}{RT}\frac{d\gamma}{da_2} \tag{3}$$

where μ_2° is the chemical potential of the solute in the standard state

*For a good discussion of this concept, see N. K. Adam, The Physics and Chemistry of Surfaces, Oxford University Press, 1941, pp. 107-113 and 404-409.

at a constant temperature, and a_2 is the activity of the solute for dilute solutions. The activity may be replaced by the concentration, C, and the approximate form

$$\Gamma_2 = -\frac{C}{RT}\frac{d\gamma}{dC} \tag{4}$$

is obtained.

If the surface phase is assumed to be only one molecule thick, at constant surface area

$$\sigma = -\frac{C}{RT}\left(\frac{\partial\gamma}{\partial C}\right)_s \tag{5}$$

where σ = number of molecules per sq. cm. Thus for the solutes that produce a lowering in surface tension, there will be a greater concentration of the solute in the surface phase than in the bulk phase.

3. Langmuir adsorption equation.--Langmuir (18) in 1916 developed relationships for the adsorption of gas molecules onto a solid surface. The Langmuir equation was derived from the consideration that a gas molecule striking a homogeneous solid surface may either rebound elastically or condense at the surface, re-evaporating after a longer or shorter time. Langmuir considered the forces involved in adsorption to be effective for very short distances only, and assumed that a molecule striking another adsorbed molecule returns immediately to the gas phase. He further assumed that the heat of adsorption will be the same for every molecule which strikes the bare surface and that this heat of adsorption is not affected by the presence of other adsorbed molecules. The first assumption leads immediately to the

conception of a layer one molecule thick as the upper limit of adsorption.

Under these limitations, consider a unit area of a homogeneous surface in contact with a single gas at some pressure, P. If the number of adsorbed molecules per unit area of surface which would completely fill the surface with a unimolecular layer is denoted by σ_o and the number of molecules which are actually adsorbed by σ, the number of places available for adsorption is seen to be $\sigma - \sigma_o$. If n molecules strike the surface every second, a fraction $\frac{\sigma}{\sigma_o}$ will strike on molecules already adsorbed and will return immediately to the gas phase. The fraction available for adsorption is therefore, $1 - \frac{\sigma}{\sigma_o}$.

It can be said then that

$$\sigma = n(1 - \frac{\sigma}{\sigma_o})\tau \tag{6}$$

where τ is the average length of time (in seconds) that an adsorbed molecule remains on the surface.

If the amount adsorbed is expressed in terms of the fraction of surface covered, the equation

$$\frac{\sigma}{\sigma_o} = \theta = \frac{n\tau}{\sigma_o + n\tau} = \frac{\frac{n\tau}{\sigma_o}}{(1 + \frac{n\tau}{\sigma_o})} \tag{7}$$

is obtained. The fraction of surface covered, θ, is proportional to the number of moles of solute adsorbed per unit area and, if equal masses are assumed to have equal surface areas, is proportional to the number of grams adsorbed (x) divided by the mass (m) of adsorbent. Thus

$$\theta = k_1 \frac{x}{m} . \tag{8}$$

From the kinetic theory of gases,

$$n = \frac{NP}{(2\pi MRT)^{1/2}} \tag{9}$$

where N is Avogadro's number, and R, P, T, and M have their usual significance. For a given gas at a particular temperature

$$n = aP \tag{10}$$

where

$$a = N(2\pi MRT)^{-1/2} . \tag{11}$$

Let

$$\frac{\tau}{\sigma_o} = b. \tag{12}$$

If equations (10) and (12) are substituted in equation (7) and combined with equation (8)

$$\theta = \frac{k_1 x}{m} = \frac{abP}{1 + abP} \tag{13}$$

and

$$\frac{x}{m} = \frac{ab}{k_1} \frac{P}{1 + abP} = \frac{ABP}{1 + AP} \tag{14}$$

where $A = ab$ and $B = 1/k_1$.

Unimolecular adsorption from solution will be represented by an equation of the form

$$\frac{x}{m} = \frac{A'B'C}{1 + A'C} \tag{15}$$

where A' and B' are constants corresponding to the constants A and B of equation (14), and C is the concentration.

The form of the Langmuir equation (or isotherm) depends upon the magnitude of A. If AP is small so that $AP << 1$, the fraction of the surface covered will be proportional to the pressure or concentration; whereas if AP is large so that $AP >> 1$, the fraction $\theta = 1$, and the unimolecular layer will be complete.

Adsorption isotherms are frequently encountered which show a tendency to reach a saturation value, assumed to be a unimolecular layer. Whether or not the shape of the isotherm actually is described by equation (14), isotherms of this type are usually referred to as being of the "Langmuir type."

For the occurrence of the adsorption phenomena described by the Langmuir equation, the most important assumption is that molecules striking other molecules already adsorbed will return immediately to the bulk phase. It is not necessary that there be absolutely no binding between the first and subsequent layers for saturation to occur; it is only necessary for the time of adsorption of molecules in a second layer to be short in comparison with the time of adsorption in the surface layer. This condition is fulfilled in cases of chemisorption and many cases of physical adsorption. It is also fulfilled when long organic molecules with a dipole on one end are adsorbed on polar surfaces. The adsorption of fatty acids on the surface of inorganic salts or oxides, or on water surfaces, would therefore be expected to give a Langmuir-type isotherm (7).

4. BET adsorption equation.--There arise situations wherein the

adsorbate molecules striking molecules already adsorbed do remain for an appreciable time. Thus, conditions for adsorption in more than one layer occur. Langmuir and others after him made attempts to derive an equation for the adsorption isotherm in the case of multilayer adsorption. The most successful attempts in this direction are due to Brunauer, Emmett, Teller, L. S. Deming, and W. E. Deming (3,4). Their theory is known generally as the BET theory.

In the development of the BET theory the following fundamental assumptions were made: (1) The area of the total adsorbing surface (adsorbent) is measured in terms of the cross-sectional area of the adsorbate molecules, and this is assumed to be the same as that in the liquid phase. (2) The first layer of adsorbed molecules is held to the adsorbent by a force which is related to the average heat of adsorption of the first layer and to the temperature. (3) The adsorptive forces that bind the first layer do not extend appreciably beyond the first layer, so that the heat of adsorption of the second and subsequent layers will be close to the heat of liquefaction of the gas.

The most familiar form of the BET equation is

$$\frac{P/P_o}{v(1 - P/P_o)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c}(P/P_o) \qquad (16)$$

where P = the equilibrium pressure,

v = volume of gas adsorbed at P,

v_m = volume of gas adsorbed when the surface is completely covered with a unimolecular layer,

P_o = vapor pressure of the liquid adsorbate, and

c = a constant involving the heat of adsorption.

A plot of $(P/P_o)/v(1 - P/P_o)$ versus P/P_o gives a straight line over the region in which this equation is valid. The intercept of this line is $1/v_m c$, and the slope is $(c - 1)/v_m c$. Thus v_m may be calculated, and from this, the surface of the adsorbent, if the average area occupied per molecule is known. Brunauer and Emmett estimate the molecular area in the monolayer from a relation involving hexagonal close packing in the liquid or solid.

The theory of multimolecular adsorption as developed by Brunauer, Emmett, and Teller has been widely criticized with various arguments. Brunauer himself gives a very fair set of criticisms in his book (5). Nevertheless, the theory has been successfully used by many investigators for the purpose of estimating the surface area of various materials; it is in fact the generally accepted standard for measuring surface area of finely divided or highly porous material.

5. Other theories.--Two other theories of interest are the potential theory and the capillary-condensation theory. The potential theory in its original form as advanced by Polanyi (30) assumed that adsorption was due to long-range attractive forces extending from the surface so that several layers, or an "atmosphere" of molecules, might be held to the surface. This, however, did not enter into the formulation of the theory, which was easily modified later to conform more nearly with the modern concepts of the nature of molecular forces. Brunauer maintains that the Polanyi theory is the only theory of physical adsorption that can handle adsorption quantitatively on a highly heterogeneous surface (5).

The capillary-condensation theory of Zsigmondy (37) attributes

adsorption to condensation of the gas in the capillaries of the adsorbent. This theory is based upon the long-known phenomenon that a liquid that wets the walls of a capillary has a lower vapor pressure in the capillary than in the normal bulk phase. Zsigmondy assumed that in very small capillaries condensation could take place at pressures considerably lower than the normal vapor pressure. Thus, at low pressures the smallest capillaries would fill with liquid; as the pressure was raised larger capillaries would be filled, and so on in this fashion till all the pores of the solid were filled with liquid. It appears that capillary condensation does play a role in many adsorption processes (28).

One finds in practically all phases of adsorption studies references to the "classical" or "Freundlich" isotherm. This isotherm is purely empirical and due not to Freundlich but to Küster (25). The classical isotherm equation can be put in the form

$$V_a = kP^{1/n} \tag{17}$$

where $n > 1$,

P = equilibrium pressure, and

V_a = volume of gas adsorbed.

For adsorption from solution this equation can be expressed as a function of concentration, C, of solute:

$$x/m = k'C^{1/n} . \tag{18}$$

6. Adsorption from solution.--The accumulation of one molecular species at the interface between a solid and a solution is governed by complex

phenomena. The molecules may accumulate at the interface as a result of interfacial tension, may attach onto the solid surface through strong chemical valence forces, or may attach onto the solid surface through relatively weak physical (van der Waal's) attractive forces.

Adsorption on a solid surface usually falls into one of two classifications, depending upon the nature of the forces existing between the solute molecules and the substrate. These two types are (1) physical or "van der Waal's" adsorption and (2) chemisorption (sometimes called "irreversible" or "activated" adsorption). The most obvious difference between the two types is in the magnitude of the heats of adsorption, which is usually less than 4000 calories per mole for van der Waal's adsorption, but much higher (generally at least 10,000, and occasionally up to 200,000 calories per mole) for chemisorption (1). In physical adsorption, the desorption isotherm is essentially the same as the adsorption isotherm; whereas for chemisorption the molecules are not easily removed by merely lowering the equilibrium concentration of the solution. Often in chemisorption, when the molecules are removed from the surface, it is found that a surface reaction has occurred; e.g., fatty acids adsorbed onto metallic surfaces may be found to be the appropriate metallic soap when desorbed.

Molecules are adsorbed on solid surfaces by interaction of the unsatisfied force fields of the surface atoms of the solid with the force fields of the molecules striking the surface. In this way the free energy of the solid surface is diminished (1). The type of interaction, if any, that occurs between the solute molecules and the solid will be dependent upon the nature of the surface and of the

solute molecules.

In adsorption from solution a complicating factor arises, that of the possibility of competition between the solvent and solute molecules for sites on the surface. Obviously when the solid is first immersed in the solution, a large part of the surface will be covered with solvent molecules, especially in dilute solutions. It must be remembered, however, that even at equilibrium the adsorbed molecules--excluding some cases of chemisorption--are not rigidly bound in place. Molecules are constantly leaving the surface and being replaced with other molecules. Under such conditions if there are present but two molecular species--with one having a much longer average "life" of adsorption, i.e., the time of adsorption is long--then there will be an accumulation at the surface of the species having the longer time of adsorption.

As already stated, the conditions encountered in adsorption from solution very often are approximated by the assumptions of the Langmuir theory. This appears to be particularly true with regard to the assumption of the formation of a unimolecular layer. Under most conditions the attraction between the molecules of the solvent and the solute molecules in the first adsorbed layer will be greater than the attraction between a solute molecule in solution and a similar molecule in the unimolecular layer. This, apart from entropy, is one of the reasons why the substance is in solution (7). For the total system, the adsorption of a second layer of solute molecules will be accompanied by a change in entropy which is approximately the same as that accompanying the adsorption of a layer of solvent molecules on top of the

first adsorbed layer.

It is to be expected that the forces associated with adsorption will vary with different faces of even a perfect crystal. With an adsorbate that was held only weakly, it is possible that while the forces of some faces would be strong enough to cause adsorption, the energy of the adsorbate molecules could be such that no adsorption would occur on other faces.

Since adsorption is an exothermic process, it would be expected that an increase in temperature would cause a general decrease in adsorption. Therefore, it appears that adsorption carried on at low temperatures would be most likely to achieve complete unimolecular coverage of the solid.

The above argument holds true for adsorption both from the gas phase and from solution. From solution another effect of temperature is encountered--that of solubility of the solute. Since the solubility of a substance determines its chemical potential, which in turn controls the adsorption, the solubility factor may be of paramount importance. Bartell, Thomas, and Fu (2) have shown excellent examples of this by measuring the adsorption from solution of substances having negative temperature coefficients of solubility. It was found that more of the substance was adsorbed for low concentrations at T_1 than at T_2, where $T_1 < T_2$; but as the concentration was increased beyond a certain point more was adsorbed at T_2, thus demonstrating that the solubility effect becomes more important than the temperature effect at concentrations well below that necessary for maximum adsorption.

CHAPTER III

INVESTIGATION AND RESULTS

A. Statement of Problem and General Approach

The problem at hand is to evaluate critically the use of the adsorption of stearic acid from solution as a means of measuring the surface area of particulate matter; to evolve, if possible, improvements to the present techniques used for this purpose; and to delineate the limitations of present techniques.

In order to get reproducible values by the BET procedure, it is imperative that the solid be completely degassed prior to adsorption measurement. For adsorption from solution, it was found by Greenhill (8) and by Russell and Cochran (33) that adsorption was essentially the same on metals, metal oxides, and non-porous alumina whether the samples were degassed or not. Gases adsorbed on the solid are apparently displaced by the liquid phase (17). The presence of water, however, has been found to initiate chemical reactions with some powders. With wet powder, Hirst and Lancaster (14) found that the amount of stearic acid taken up by Cu, Fe, Cu_2O, and CuO was many times the amount required to give a monolayer at 18° C.

The time required for equilibrium to be reached in the adsorption of fatty acids from solution has been reported to be very short. Greenhill (8) found that for the adsorption of stearic acid on various metals from benzene, approximately 90 per cent of the amount adsorbed in four hours occurred in the first five minutes. Smith and Fusek (34),

working with palmitic acid in benzene and a platinum catalyst, found that the maximum amount adsorbed occurred in less than an hour.

Adsorption isotherms are usually presented as a plot of the amount of acid adsorbed against the absolute concentration, C, of the solution. Hirst and Lancaster (15) have suggested plotting, as abscissa, the relative concentration, C/C_o, where C_o is the saturation concentration. These authors showed that for adsorption of stearic acid in benzene on TiO_2, SiO_2, TiC, and SiC, essentially the same curve was obtained by (1) varying C while keeping the temperature (and hence C_o) constant or (2) varying the temperature (and therefore C_o) while keeping C constant. This is in keeping with the result obtained by Heyne and Polanyi (12), that the variation with temperature of the limiting amount adsorbed from solution is small.

An interesting fact brought out by isotherms plotted in this manner is that in practically every case, the maximum amount of adsorption has occurred at fairly low values of the relative concentration. Figures 9 through 14 show adsorption data plotted in this manner. Since in all cases the amount adsorbed reaches a maximum in the neighborhood of relative concentration values of 0.2 to 0.3 and remains essentially constant thereafter, it could be expected that single-point determinations at values above this would, in most instances, give the maximum amount of acid adsorbed. If this observation is valid, then to determine the surface area it is necessary to make only one adsorption measurement, adjusting the amount of adsorbent and solution concentration to such values that the equilibrium concentration will not be below a relative value of 0.3.

The general approach to the problem consisted of determining the extent of adsorption on a dried but not evacuated solid. If the values so obtained differed substantially from those obtained by the BET procedure, the sample was heated and evacuated to determine if better results were thereby obtained. For those cases in which the relative concentration at equilibrium was below 0.3, the adsorption was redetermined at higher values of C/C_o.

For such a study, it is obvious that an accurate analytical procedure for determining the amount of stearic acid in solution is mandatory. A great deal of preliminary work was devoted to an appraisal of the various techniques used for this purpose.

A number of investigators have determined the amount of acid in solution by evaporating an aliquot of the solution to dryness, and weighing. Russell and Cochran (33) found that slight amounts of the stearic acid also were lost due to evaporation, so that a correction was necessary to compensate for this loss. Smith and Fusek (34), however, reported good results with this procedure. While the errors due to loss of acid may not be too great--0.5 to 1.0 per cent--the time required for such an analysis is excessive (usually three or four hours).

B. Analytical Procedures

1. Refractometric and spectrophotometric techniques.--An attempt was made to determine the concentration change by use of a dipping refractometer. This instrument was not sensitive enough to detect small changes in concentration. No significant absorption frequency was

found in the range 200 to 1000 millimicrons on the Beckman model D spectrophotometer. A similar lack of success was encountered in the use of a flame photometer in conjunction with the Beckman model B spectrophotometer. The colorimetric procedure, proposed by Hill (13), which involves the formation of a ferric hydroxamate complex with the fatty acid was found to have an accuracy of ± 6 per cent, an error large enough to obscure completely adsorption results in many instances.

2. Conductometric technique.--The conductometric method of Maron, Ulevitch, and Elder (23) was found to be satisfactory from the standpoint of accuracy as well as speed. This technique consisted of titrating the stearic-acid sample in 100 ml. of a 50 per cent mixture of water and isopropyl alcohol. The mixture was titrated with 0.1 N NaOH solution.

The NaOH solution was prepared by dilution of carbonate-free base with distilled water which had been run through a three-foot ion-exchange column. The NaOH was standardized against potassium acid phthalate with phenolphthalein indicator.

After the addition of small volumes of NaOH, the resistance of the acid-alcohol solution was measured by use of an Industrial Instruments, Inc., model RC-1 conductivity bridge with platinized platinum electrodes. The mixture was agitated during titration by means of an electric-driven stirrer. The titration cell was provided with a cover to prevent excessive contact of the solution with the air. The apparatus is shown in Figure 4. The alcohol-water mixture showed a blank consumption of 0 to 0.003 milli-equivalents of NaOH per ml. of mixture. This value was a characteristic of the alcohol, varying from batch to batch. The reciprocal of the measured resistivity was plotted against the volume of NaOH

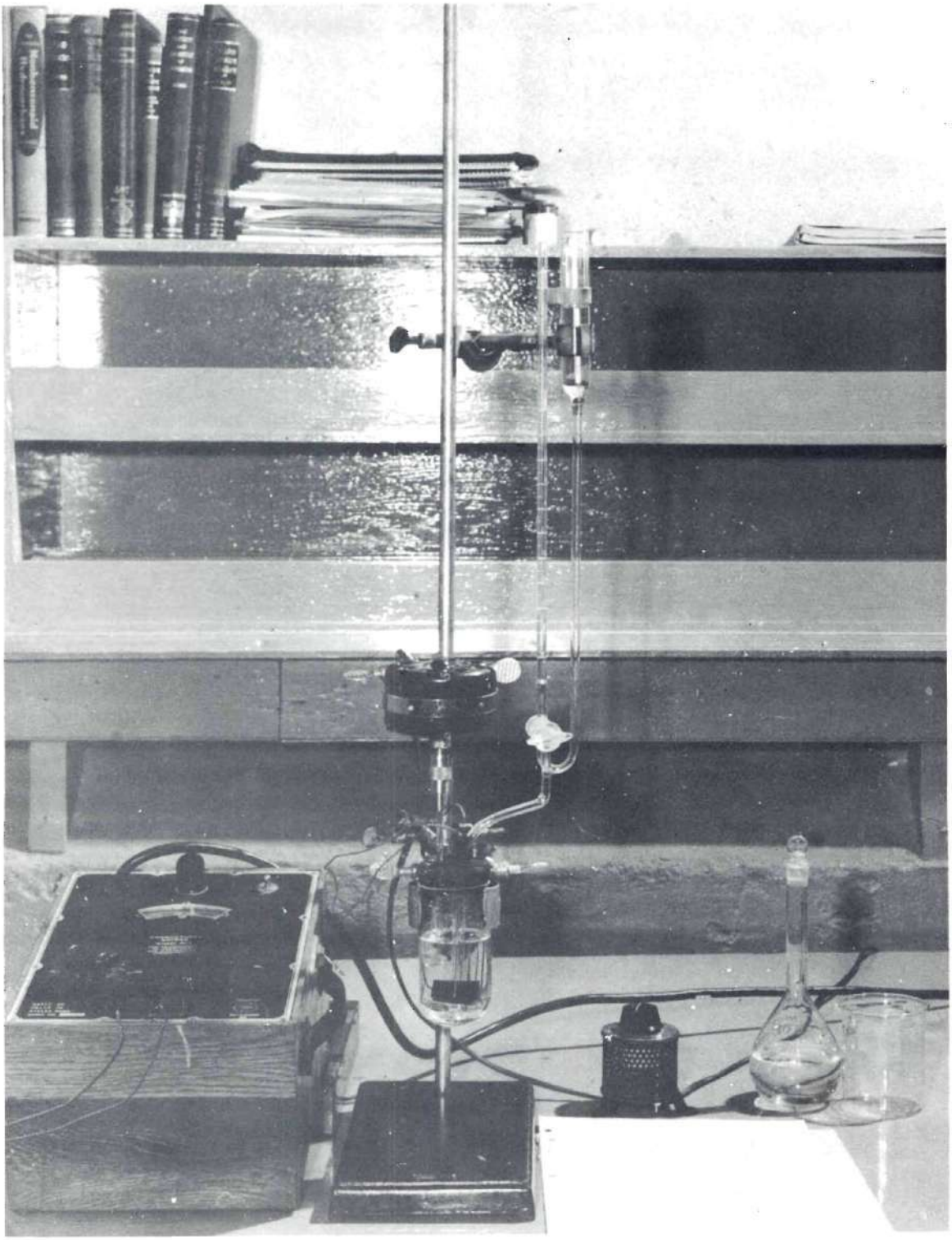

Figure 4. Conductometric Titration Apparatus.

added. The end-point of the titration is indicated by the intersection of the resulting straight lines. A typical plot is shown in Figure 5. From titration curves of solutions of known concentration the error of this analytical procedure was found to be 2 per cent or less.

3. Langmuir trough technique.--It was subsequently found that the use of a Langmuir trough was even more satisfactory as a means of measuring the residual acid concentration. This method has been used by Hutchinson (16), Greenhill (8), and others for measuring the amount of fatty acid in solution. The Langmuir trough, or hydrophil balance as it is sometimes called, is shown in Figure 6. It consists essentially of an accurately machined tray provided with a fixed barrier and a movable barrier. A Central Scientific Company balance, Cat. No. 70531, was used in this investigation.

In use, the tray is carefully leveled and filled with water or other liquid so that the meniscus stands well above the surface of the edges. The solution to be measured is placed on the cleaned water surface and the solvent allowed to evaporate. Advancing the movable barrier compresses the molecules floating on the surface, since they are confined between the two barriers. The fixed barrier is attached to a torsion wire mounted in a frame on the tray; thus the force exerted on the barrier may be determined. The ends of the fixed barrier are connected to the edges of the trough by small flexible strips--usually of platinum. These strips do not exert any appreciable drag on the barrier, yet prevent the surface film of fatty-acid molecules from slipping past.

The usual practice is to coat the tray with several layers of

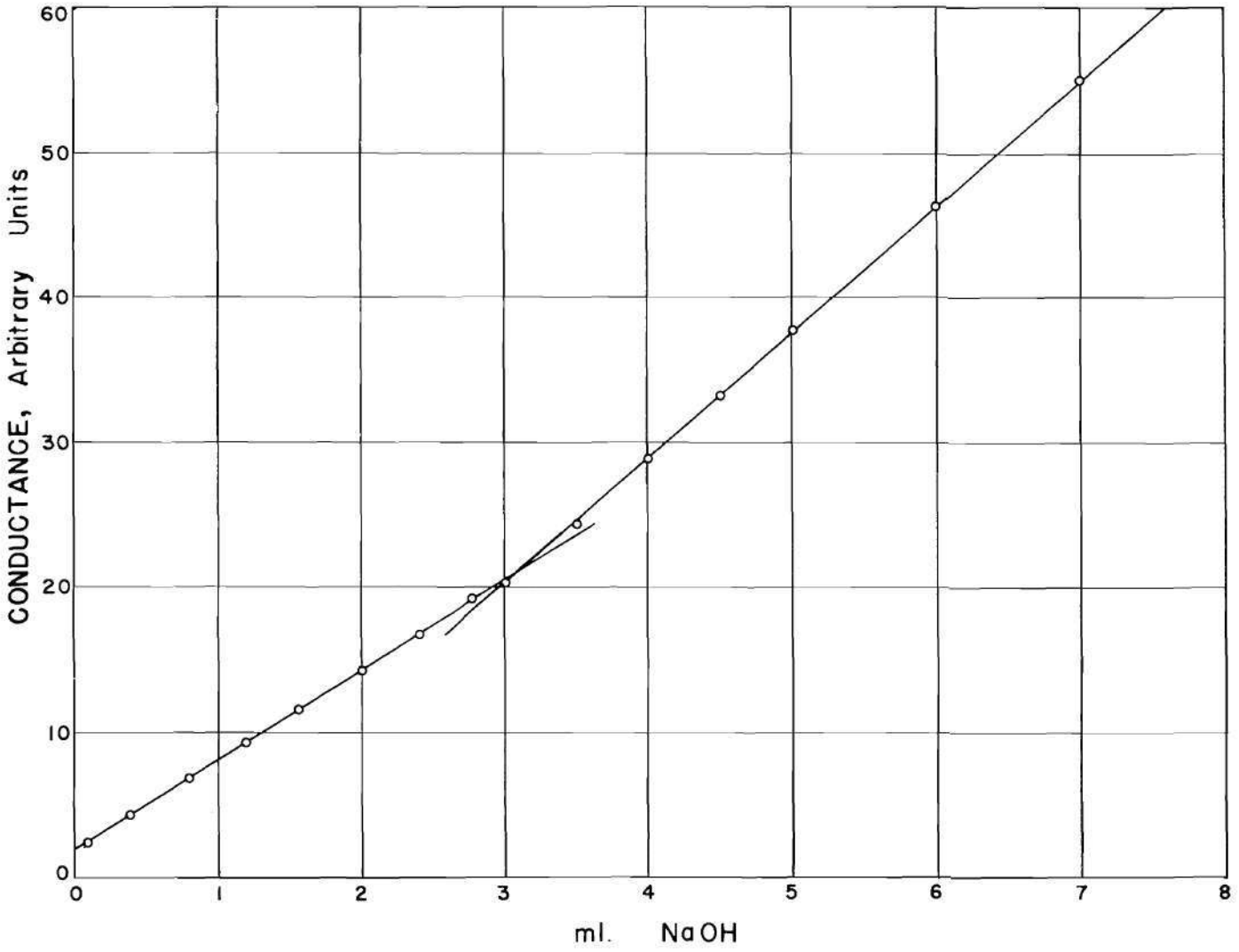

Figure 5. Typical Plot of Conductometric Titration of Stearic Acid with NaOH.

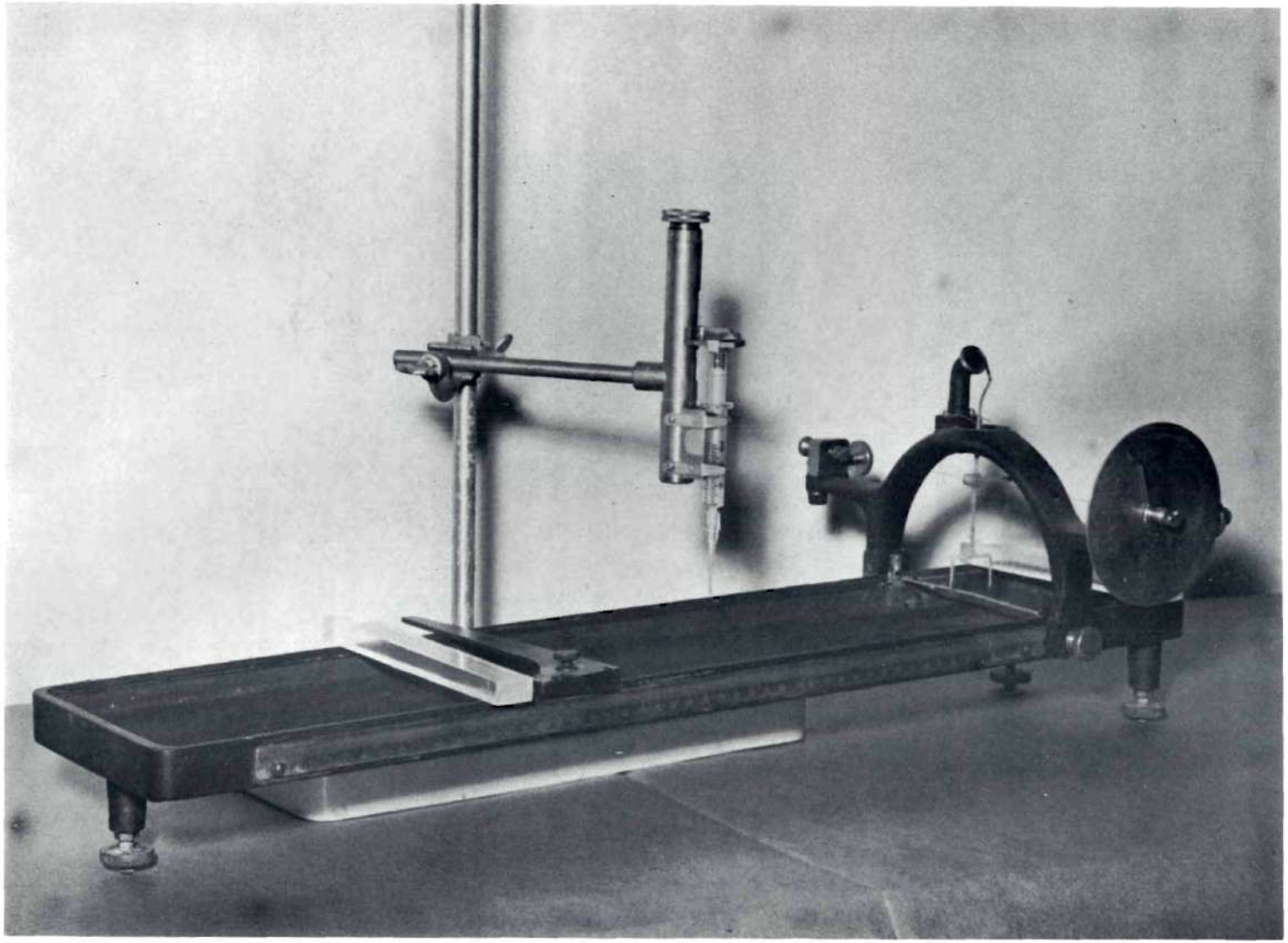

Figure 6. Langmuir Trough.

paraffin or other wax. This serves a twofold purpose: (1) the meniscus of the water will stand much higher without danger of overflowing, and (2) the molecules of acid in the surface film are thus prevented from adsorbing to, or otherwise reacting with, the metal surface, thereby causing erroneous results. It was found in this study that the wax coating was conducive to errors, due to the fact that some of the solvents used dissolved small portions of the wax. When the solvent evaporated, the film of wax behaved just like the acid film. To overcome this difficulty the tray was coated with seven, two-mil coats of DuPont TEFLON, which has all the advantages of the wax coating with none of the disadvantages. The platinum strips were replaced with TEFLON strips 0.001-inch thick. These were more flexible and caused less trouble than the coated platinum strips.

In analyzing for the amount of acid present most workers follow the procedure of Hutchinson (16) and Greenhill (8), i.e., a known volume of solution is spread on the balance, and the barrier is moved up until the film is under a predetermined pressure. From a knowledge of the pressure-area relationship of the fatty acid film (see Chapter II), the amount of acid on the surface can be calculated. This procedure requires that the torsion wire be very accurately calibrated and that the temperature of the entire system be closely controlled. Figure 2 shows the pressure-area relationship for stearic acid on 0.01 N hydrochloric acid. The effect of temperature on the molecular area of palmitic acid film on hydrochloric acid is seen in Figure 7, which shows that although in certain ranges the temperature effect is small, in others it may be very appreciable.

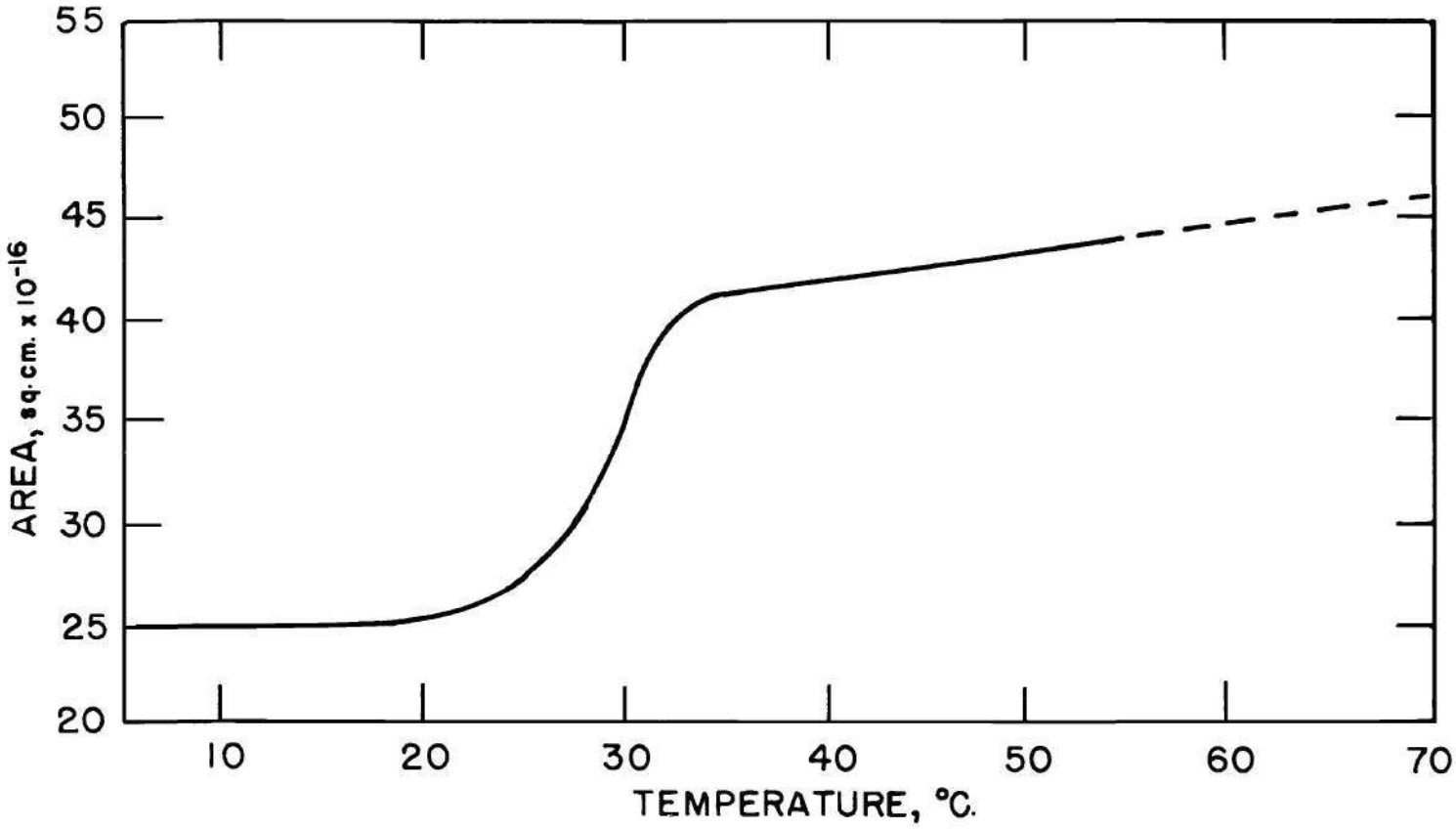

Figure 7. Effect of Temperature on Molecular Area of Palmitic Acid in Monomolecular Film.*

*Data from Markley (22).

In order to avoid the above-mentioned difficulties, a comparison method of analysis was used. With the torsion head set at such an angle that it would produce a force of approximately 25 dynes per centimeter, a volume of known concentration was spread upon the surface. After the solvent had evaporated, the film was compressed till the float indicator was at the null position, and the distance between the movable barrier and the float was noted. The surface was then swept clean, and the same volume of unknown concentration was spread on the surface. Since the width of the tray was uniform, the ratio of the distances between the float and the movable barrier for the different cases was the same value as the ratio of the two concentrations. The error of analysis of this procedure was found by measurement of known solutions to be less than 1 per cent.

C. Experimental Procedure and Sample Calculations

The experiments in this study were conducted with solids that had been dried in a vacuum oven for at least two hours at 20 in. Hg. vacuum and 110° C. The dried material was weighed into a suitable container. Early work was done with stoppered 150-ml. Erlenmeyer flasks. It was found that the loss of solvent by evaporation during the experiment in some cases was appreciable, and the use of screw-cap test tubes proved to be more satisfactory. The liners of the caps were removed and replaced with cork-backed TEFLON liners which afforded a very tight seal and also prevented the contamination of the solution due to any slight solubility of the plastic liners in the solvents used.

To the dried material in the test tube, a measured amount of stearic acid solution was added. The container was mounted in a Burrell

model CC "wrist-action" shaker in such a manner that it was surrounded by the thermostatically controlled bath.

The fluid in the bath was circulated through an external coil placed in an alcohol-ice bath. Temperature control was effected by cooling the fluid well below the desired value in the external coil and heating inside the bath with submerged resistance heaters which were controlled by a temperature regulator, Precision Scientific Company Cat. No. 6530. The fluid in the bath was agitated by an electrically driven stirrer. This equipment is shown in Figure 8. With this apparatus, the temperature was maintained within 0.2° F. of the set value. Some of the experiments were conducted at room temperature without the use of the thermostatically controlled bath.

After the mixture was shaken for at least an hour, the solids were allowed to settle, and an aliquot of the supernatant liquid was withdrawn for analysis of the stearic acid present. To illustrate the step-by-step procedure, a sample run and calculation is presented below.

Sample Calculation

System: TiO_2--stearic acid in benzene

The TiO_2 was dried in a vacuum oven at 105° C. and 29.5 in. Hg. vacuum for two hours. The sample was weighed into a screw-cap test tube and 10 ml. of stearic-acid solution added. The sample tube was then placed in a thermostated bath and shaken for one hour at 76° F. After the solids had settled, five ml. of the solution was removed for analysis. This was diluted with an equal volume of

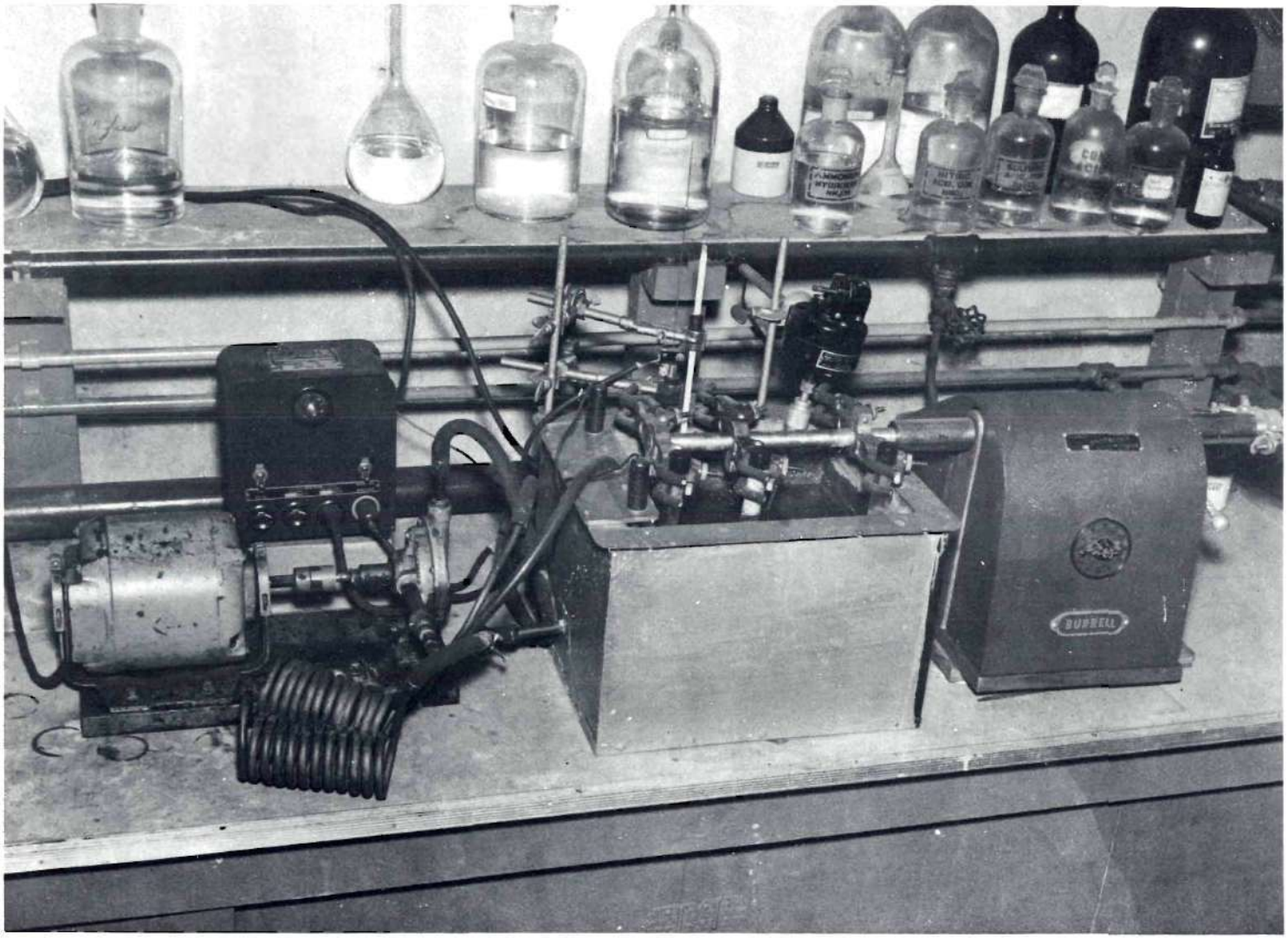

Figure 8. Thermostated Bath and Shaker.

benzene, and approximately* 0.2 ml. was spread on the water surface of the Langmuir trough by means of a micropipette. The area covered by the film was measured at 25 dynes/cm. surface pressure. Approximately six such readings were made for each analysis, the mean being compared with the mean of a similar number of readings obtained for the same volume of a known concentration. The readings for the known solution were obtained each time an analysis was made, since this value may change slightly from time to time. Since the amount of acid present in solution before and after adsorption was known, it was possible to calculate the surface area by assuming that the film was close-packed and the cross-sectional area per adsorbed molecule was 20.5 Å^2.

Data:

Weight of TiO_2 sample	1.4921 g.
Benzene-stearic acid solution added to sample	10.00 ml.
Initial stearic acid concentration in benzene solution	17.0000 g./ℓ.
Trough reading for blank	38.7 cm.
Trough reading for sample	32.4 cm.

*The word "approximately" does not imply that the volume delivered to the surface is not accurately known. It may be necessary to vary the amount slightly by 0.010 ml. or so in order that a large droplet will not be left on the delivery tip of the pipette, for in such an event the droplet may release at one time and not another, thereby giving rise to errors. The exact amount delivered will vary with the delivery tip being used. It is imperative that the same volume of known concentration as that of unknown concentration be spread on the surface in the comparative method of analysis used here.

Calculations:

Benzene-stearic acid concentration after adsorption:

$$\frac{32.4 \text{ cm.}}{38.7 \text{ cm.}} \times 17.0000 \text{ g./}\ell. = 14.2324 \text{ g./}\ell.$$

Stearic acid adsorbed:

$$\frac{10}{1000} \times (17.0000 - 14.2324) \text{ g./}\ell. \times \frac{1 \text{ mole}}{284.5 \text{ g.}} = 0.9727 \times 10^{-4} \text{ moles}$$

Specific surface area of sample:

$$\frac{0.9727 \times 10^{-4} \text{ moles}}{1.4921 \text{ g. sample}} \times \frac{6.023 \times 10^{23} \text{ molecules}}{\text{mole}} \times \frac{20.5 \times 10^{-20} \text{ m}^2}{\text{molecule}}$$

$$= 8.04 \text{ m.}^2\text{/g.}$$

C_o at 76° F. = 5.1 g./100 g. benzene = 44.6 g./ℓ.

Relative concentration $\frac{C}{C_o} = \frac{14.2}{44.6} = 0.32$

The procedure using the conductometric titration was similar to the above, except that more solution was ordinarily used, since the volume required for analysis was much greater. A calculation illustrating the use of this type of analysis is shown below.

System: Iron--stearic acid in methanol

Data:

Iron sample weight . . . . . 10.0319 g.

Pure methanol blank requirements . . . . . 0.011 ml. NaOH per ml.

Initial stearic acid-methanol solution concentration . . . . . 0.6242 g./ℓ.

Volume of initial solution added to sample . . . 100.0 ml.

Volume of aliquot of final stearic-acid methanol solution removed from sample . . . 25.0 ml.

Volume pure methanol added to aliquot . . . . . 100.0 ml.

Normality of NaOH solution . . . . . 0.0191 N

Volume of NaOH to titrate final aliquot . . . . . 3.50 ml.

Calculations:

NaOH to saponify stearic acid in aliquot:

$$3.50 - (100.0 + 25.0)(0.11) = 2.12 \text{ ml.}$$

Stearic acid present before adsorption:

$$(100/1000) \times 0.6242 \times 1/284.5 = 21.54 \times 10^{-5} \text{ moles}$$

Stearic acid remaining after adsorption:

$$100/25 \times 2.12 \times 1.91 \times 10^{-5} = 16.20 \times 10^{-5} \text{ moles}$$

Stearic acid adsorbed:

$$(21.54 - 16.20) \times 10^{-5} = 5.34 \times 10^{-5} \text{ moles}$$

Specific surface area of sample:

$$5.34 \times 10^{-5}/10.0319 \times 6.023 \times 10^{23} \times 20.5 \times 10^{-20} = 0.66 \text{ m}^2/\text{gm.}$$

For those samples where degassing was necessary, the procedure was only slightly different. The sample was weighed in a special sample tube which had a tapered ground-glass top. The tube was fitted to the vacuum system and the sample heated by means of a heating

coil. After the sample had been evacuated to the desired pressure and held at this pressure for at least one hour, the stopcock to the vacuum system was closed. The stopcock to the solvent reservoir was then opened, so that the solid was covered with solvent without exposure to the air. The sample tube was then removed and stearic acid solution added. The sample tube was stoppered with a ground-glass stopper and placed in the shaker. From this point on the procedure above was followed.

The BET measurements were made in the Micromeritics Laboratory of the Engineering Experiment Station, Georgia Institute of Technology. The accuracy of these measurements made by this procedure are reported to be 15 per cent with a reproducibility of 5 per cent.

D. Results

Adsorption values were determined up to relative concentrations of approximately 0.7 for the solids: iron, nickel, titanium dioxide, and the ASTM kaolin. The adsorption of stearic acid by these solids was measured from solution in methyl alcohol, cyclohexane, benzene, and hexane. The isotherms were determined by measuring the adsorption from various equilibrium concentrations at 20° C. The results obtained are shown in Figures 11 through 14.

The results obtained are generally in good agreement with the BET results. The ASTM kaolin values are seen to be quite low, however. This sample was re-determined after evacuating to 0.1-micron pressure and heating to 150° C. with somewhat better results, although still lower than the BET value. It was found that after the sample was heated to temperatures much above 150° C. the sample turned black

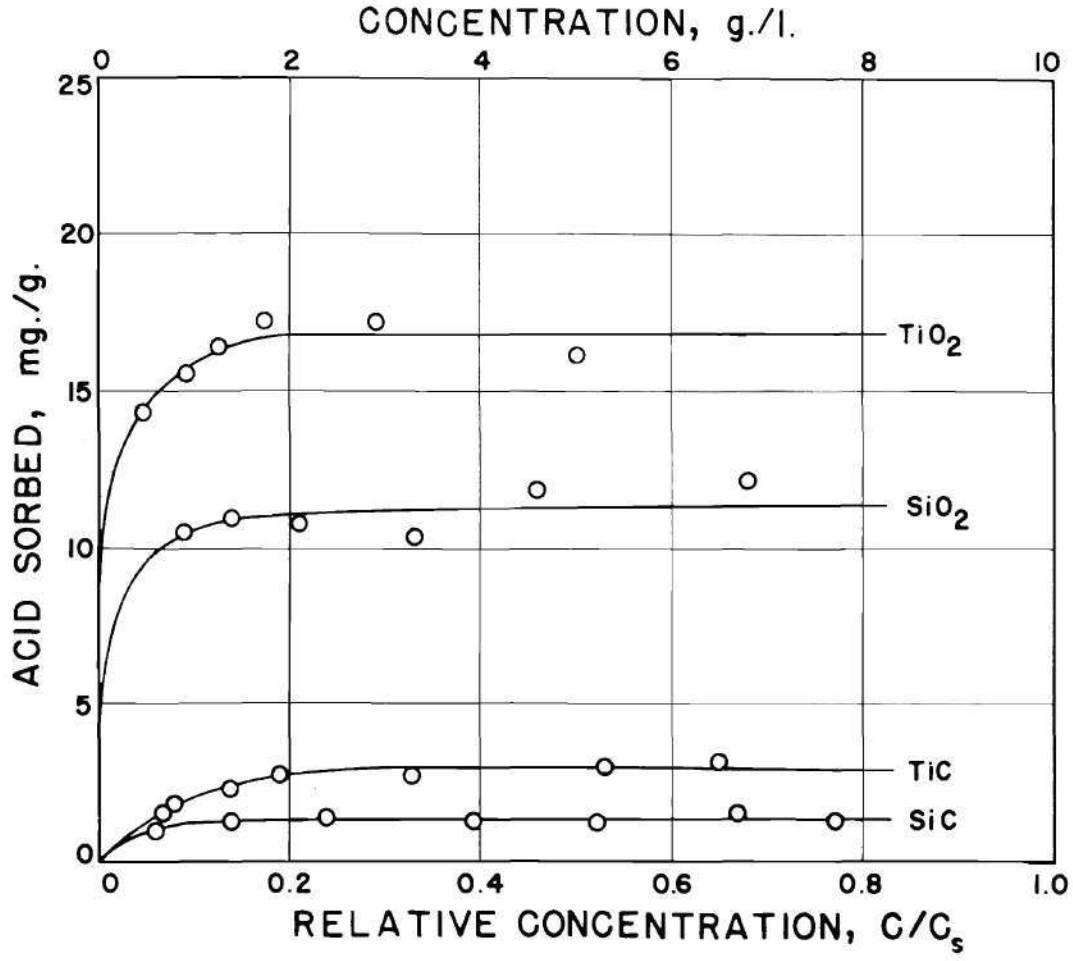

Figure 9. Adsorption of Stearic Acid From Benzene Solution on Various Solids.*

*Data of Hirst and Lancaster (14).

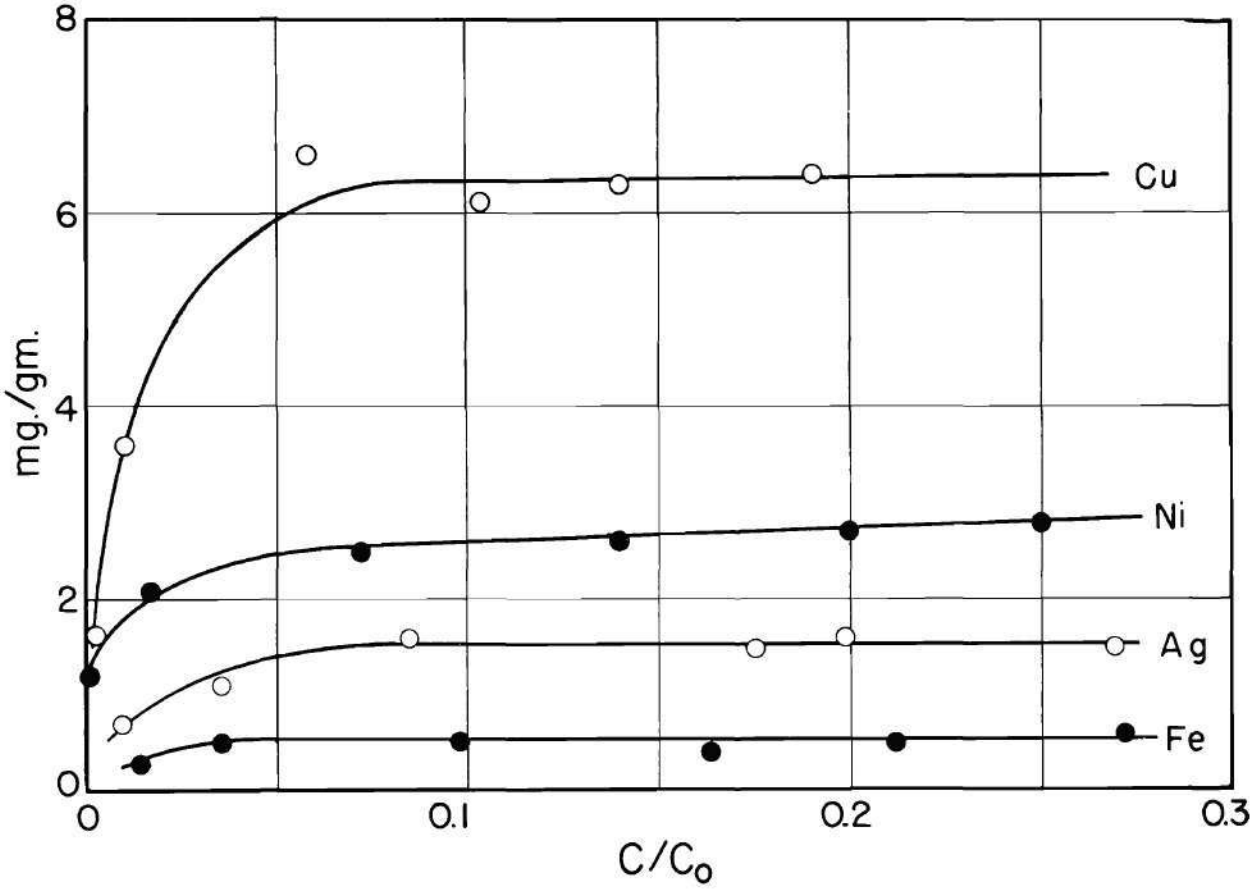

Figure 10. Adsorption of Stearic Acid From Benzene Solution on Various Metals.*

*Calculated from the data of Greenhill (8).

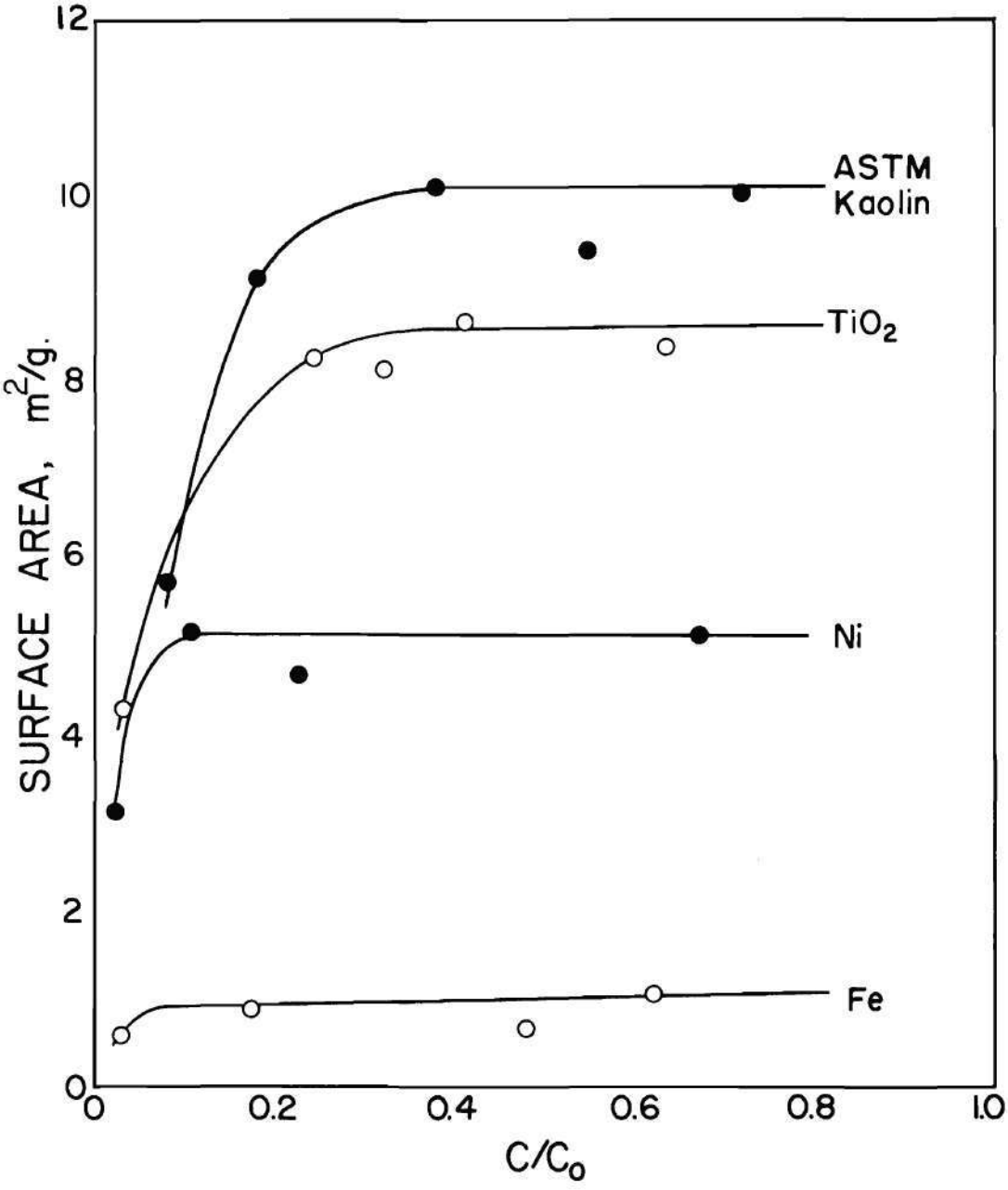

Figure 11. Adsorption of Stearic Acid from Benzene Solution on Various Solids.

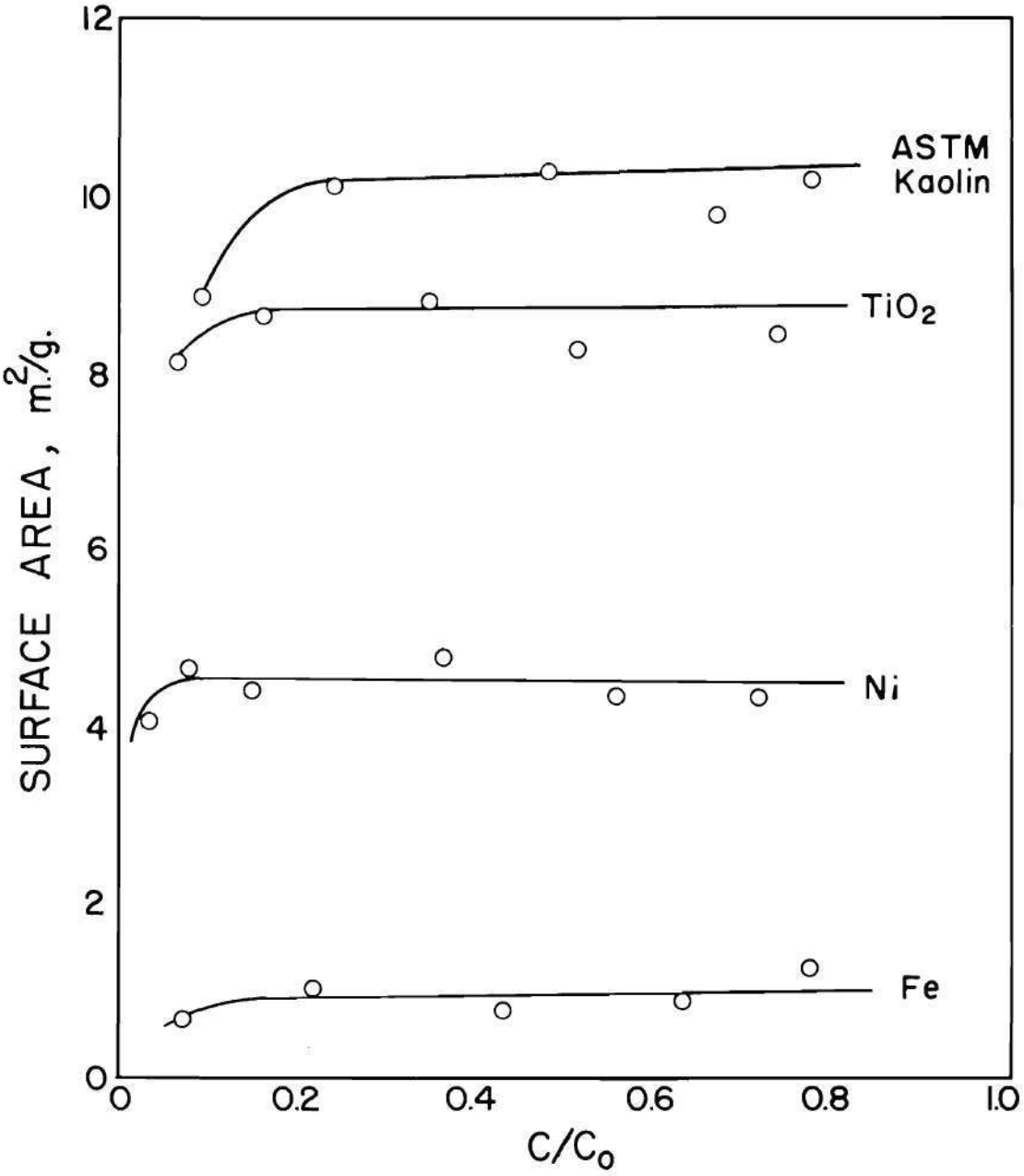

Figure 12. Adsorption of Stearic Acid From Cyclohexane Solution on Various Solids.

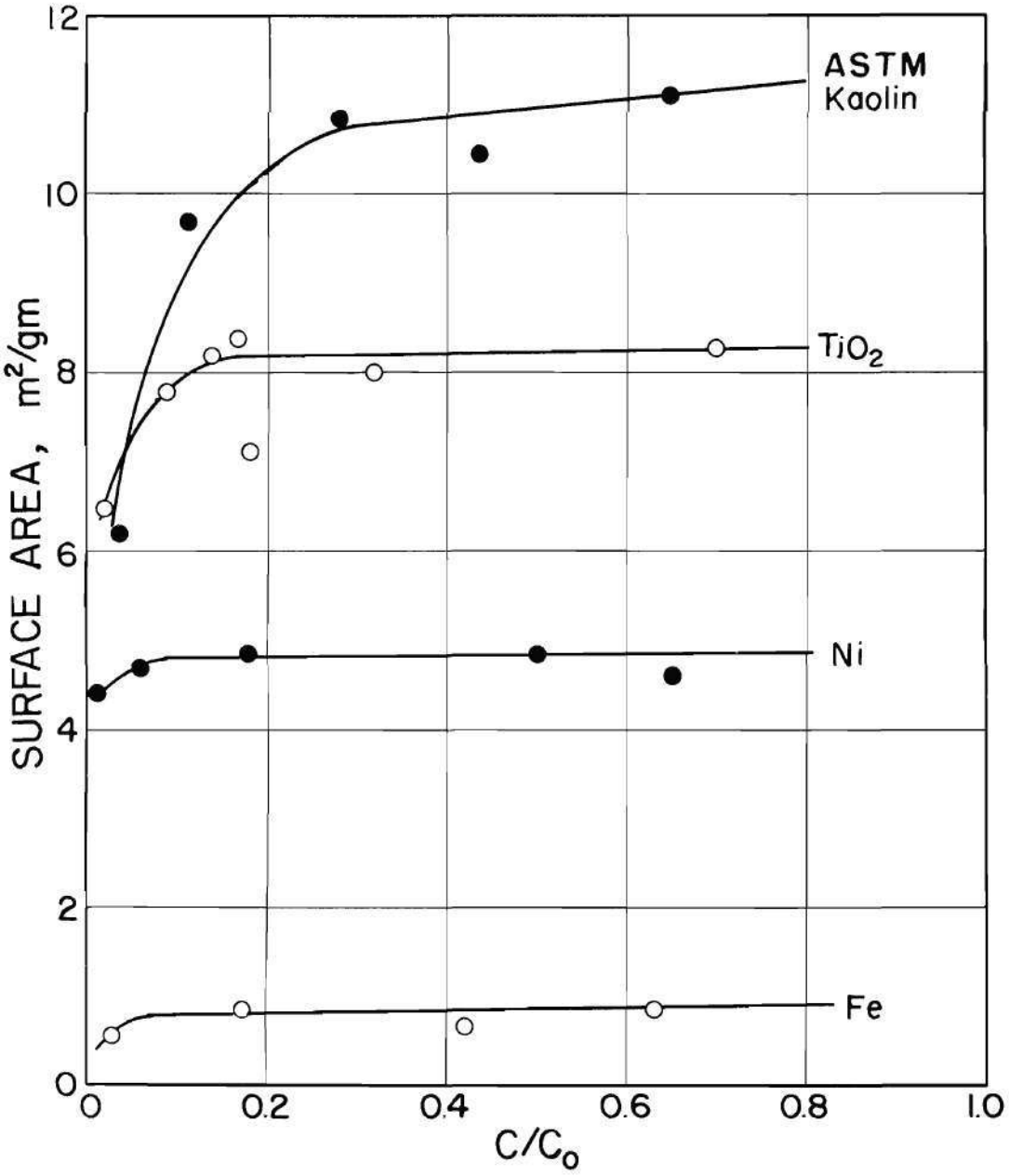

Figure 13. Adsorption of Stearic Acid From Methanol Solution on Various Solids.

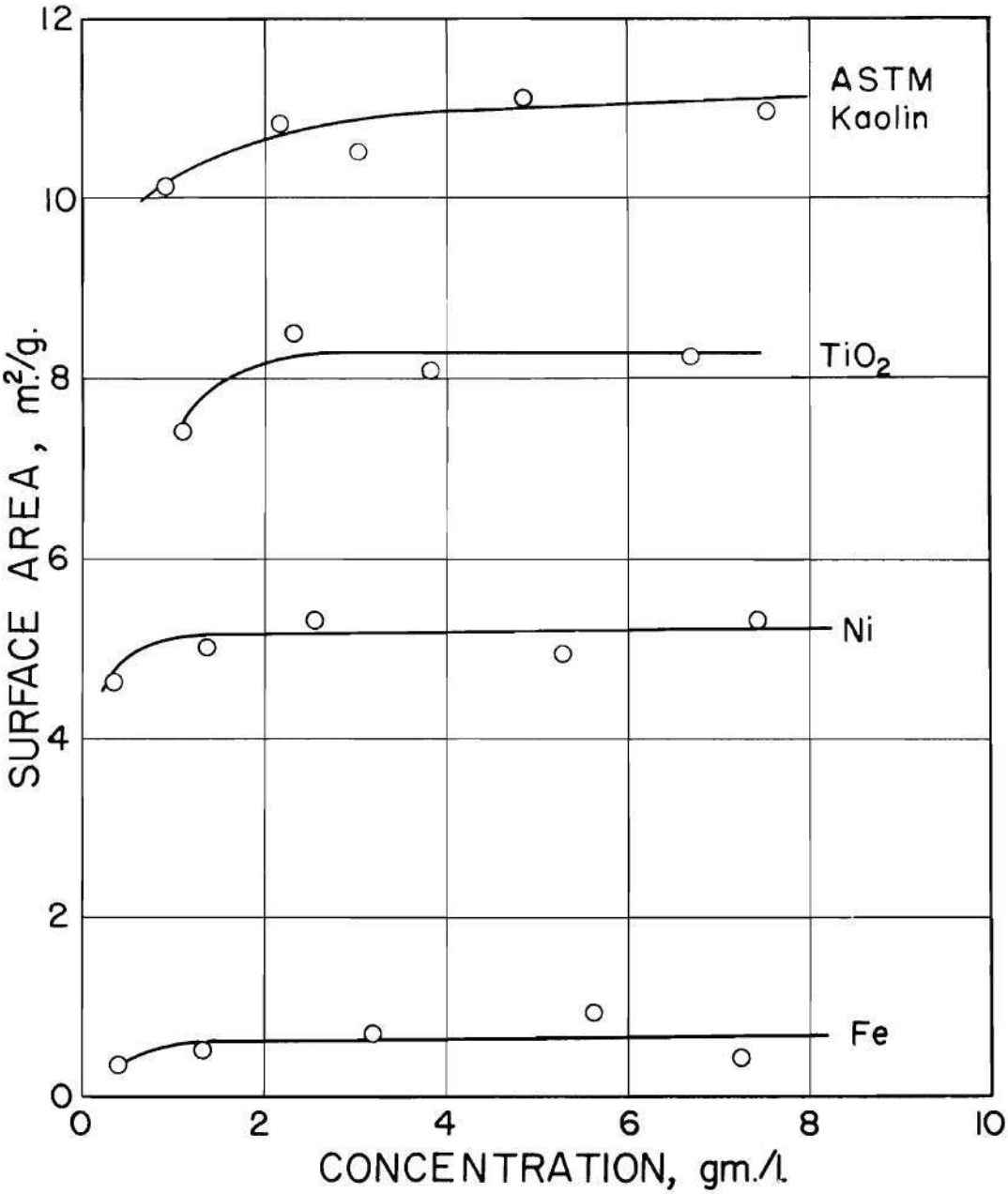

Figure 14. Adsorption of Stearic Acid From Hexane Solution on Various Solids.

when exposed to air or to the solution. Washing the sample with benzene and carbon tetrachloride produced no significant change in the value obtained.

The effect of the various solvents on the adsorption of stearic acid on the materials studied does not appear to be significant. The adsorption values for a variety of materials are shown in Table I. A number of these values were determined from one-point values; i.e., the complete isotherm was not determined. If the result obtained was appreciably different from the BET value, the extent of adsorption was redetermined after cleaning the sample surface by heating and evacuating to a pressure of 0.1μ or lower.

Reproducibility was found to be about 15 per cent as determined by a number of measurements on TiO_2. Aside from adsorption considerations, the matter of sampling of the solid was found to be quite important. The reason for this is illustrated in Figure 15, which shows a very large variation in particle sizes for the ASTM kaolin.

The adsorption data shown in Figure 10 were calculated from results obtained by Greenhill (8). If the ordinate values, (x/m), are multiplied by the area covered by a milligram of stearic acid, the surface areas of the materials would be obtained. These data and the data obtained in this investigation show that the relative concentrations at which the maximum adsorption of stearic acid occurs are appreciably lower for metals than for the other substances measured. This would indicate that the adsorption forces between metals and stearic acid are somewhat stronger than the forces between stearic acid and the other materials studied.

TABLE I

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Equilibrium Concentration Relative (C/C_o)	Equilibrium Concentration Absolute (g./l.)	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	Surface Area ($m^2/g.$) BET
1	Nickel	Benzene	0.02		3.1	5.8
			0.10		5.1	
			0.23		4.6	
			0.67		5.1	
		Cyclohexane	0.04		4.1	
			0.08		4.6	
			0.15		4.2	
			0.36		4.8	
			0.56		4.4	
			0.72		4.3	
		Methanol	0.01		4.4	
			0.06		4.5	
			0.18		4.8	
			0.50		4.9	
			0.65		4.6	
		Hexane		0.3292	4.6	
				1.3682	5.0	
				5.2545	5.3	
				2.5100	4.9	
2	Iron Powder	Benzene	0.03		0.59	0.91
			0.17		0.88	
			0.48		0.62	

(continued)

TABLE I (Continued)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Equilibrium Concentration Relative (C/C_o)	Equilibrium Concentration Absolute (g./l.)	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	Surface Area ($m^2/g.$) BET
2	Iron Powder	Benzene	0.62		1.0	
		Methanol	0.02		0.58	
			0.17		0.82	
			0.41		0.63	
			0.63		0.82	
		Cyclohexane	0.07		0.62	
			0.22		1.0	
			0.43		0.79	
			0.77		1.2	
		Hexane		0.4089	0.34	
				1.3111	0.48	
				3.1947	0.68	
				7.2274	0.42	
3	ASTM Kaolin	Benzene	0.08		5.7 **	22.8
			0.18		9.2 **	
			0.38		10 **	
			0.72		10 **	
			0.54		9.4 **	
		Methanol	0.04		6.2 **	
			0.11		9.7 **	
			0.27		11 **	
			0.44		10 **	

(continued)

TABLE I (Continued)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Equilibrium Concentration Relative (C/C_o)	Equilibrium Concentration Absolute (g./l.)	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	Surface Area ($m^2/g.$) BET
3	ASTM Kaolin	Methanol	0.62		11 **	
		Cyclohexane	0.09		8.8 **	
			0.24		11 **	
			0.48		12 **	
			0.67		9.8 **	
			0.78		10 **	
		Hexane		0.8853	10 **	
				2.1912	11 **	
				3.0101	10 **	
				4.8250	11 **	
				7.5031	11 **	
4	Titanium Dioxide	Benzene	0.03		4.2	8.07
			0.25		8.2	
			0.32		8.4	
			0.41		8.3	
			0.64		8.0	
		Cyclohexane	0.07		8.1	
			0.16		8.6	
			0.35		8.8	
			0.52		8.2	
			0.74		8.4	
		Methanol	0.01		6.5	

(continued)

TABLE I (Continued)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Equilibrium Concentration Relative (C/C_o)	Equilibrium Concentration Absolute (g./l.)	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	Surface Area ($m^2/g.$) BET
4	Titanium Dioxide	Methanol	0.09		7.8	
			0.14		8.2	
			0.17		8.4	
			0.18		7.0	
			0.32		8.0	
			0.70		8.2	
		Hexane		1.0845	7.4	
				2.2797	8.5	
				3.8069	8.1	
				6.6621	8.2	
5	Georgia Umber	Methanol	0.24		126	126
			0.17		136	
6	Kentucky O. M. #4	Methanol	0.17		13	15.4
			0.58		14	
7	Vallander	Methanol	0.10		24	24.3
			0.10		25	
			0.11		27	
8	Alabama Fire Clay	Methanol	0.10		19	13.4
			0.10		13	
9	Bentonite	Methanol	0.69		20	19.8
			0.54		16	
10	Georgia Kaolin 785	Methanol	0.37		16	21.4

(continued)

TABLE I (Continued)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Relative Concentration at Equilibrium***	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	BET
11	Georgia Kaolin 788	Methanol	0.32	15	17.6
12	Georgia Kaolin 789	Methanol	0.53	6	6.4
13	Georgia Kaolin 819	Methanol	0.13	17	14.4
14	Georgia Kaolin 858	Methanol	0.44	20	47.8
15	Georgia Kaolin 859	Methanol	0.12	49	47.8
16	Georgia Kaolin 860	Methanol	0.32	32	28.6
17	Georgia Kaolin 861	Methanol	0.37	17	16.3
18	Abrasive Alumina	Methanol	0.36	2.3	2.19
			0.34	2.3	
			0.47	2.1	
19	Adsorbent Alumina	Methanol	0.28	167	195
			0.13	182	
			0.41	172	
			0.39	197	
20	Potassium Perchlorate	Methanol	0.82	0.64	1.15
			0.84	0.65	
21	Iron Oxide	Methanol	0.37	3.6	3.53
			0.35	3.0	
22	Tungsten Carbide	Methanol	0.48	0.11	0.13
23	Tantalum Carbide	Methanol	0.43	0.09	0.09
24	Zinc Powder	Methanol	0.21	0.69	0.38
			0.28	0.43	

(continued)

TABLE I (Continued)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Relative Concentration at Equilibrium***	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	BET
25	Iron Powder	Methanol	0.17	0.85	0.78
			0.15	0.88	
			0.35	0.62	
			0.40	0.66	
26	Titanium Dioxide	Methanol	0.17	8.3	9.40
			0.19	8.2	
			0.14	8.2	
27	Copper Powder	Methanol	0.46	0.23	0.24
28	Copper Powder	Methanol	0.43	0.34	0.36
29	Nickel	Methanol	0.18	24	23.7
			0.40	24	27.4
30	Nickel	n-Propanol		7.6	15.2
31	Nickel	n-Propanol		2.6	4.5
32	Nickel	n-Propanol		5.(	5.8
33	Georgia Kaolin 860	Benzene	0.40	24.1	28.8
34	Georgia Kaolin 861	Benzene	0.50	16.1	16.3
35	So. Clay Co. Kaolin WHRM-24	Methanol	0.48	3.6	13.1
			0.51	3.8 **	
		Benzene	0.51	2.6	
			0.61	3.5 **	
			0.46	3.7 **	
36	ASTM Kaolin	Benzene	0.63	3.8	22.8
			0.47	4.6	

(continued)

TABLE I (Concluded)

SURFACE AREA VALUES BY STEARIC ACID ADSORPTION

Item No.	Material	Solvent	Relative Concentration at Equilibrium***	Surface Area ($m^2/g.$) Stearic Acid Adsorption*	BET
36	ASTM Kaolin	Benzene	0.30	5.3	
37	Abrasive Alumina	Benzene	0.62	1.2	5.1
			0.44	1.8 **	
			0.59	1.2	
38	Potassium Perchlorate	Benzene	0.43	0.13	0.11
			0.30	0.14	
			0.46	0.12	
			0.45	0.14	
39	Iron Oxide	Benzene	0.42	3.4	3.53
			0.42	3.7	
40	Copper Powder	Benzene	0.24	0.22	0.24

* Unless otherwise indicated, sample preparation consisted of drying in a vacuum oven at a temperature of 110° C. and an absolute pressure of 1 inch Hg. or less for at least 2 hours.

** Sample preparation consisted of heating at 110° C. at a pressure of 0.1 micron or lower for one hour or more.

*** The temperature was not recorded for items 5 through 29. The relative concentrations were calculated using the saturation value corresponding to 85° F. Very few of the runs were made at temperatures as high as 85°; therefore, the relative concentration values will in general be low.

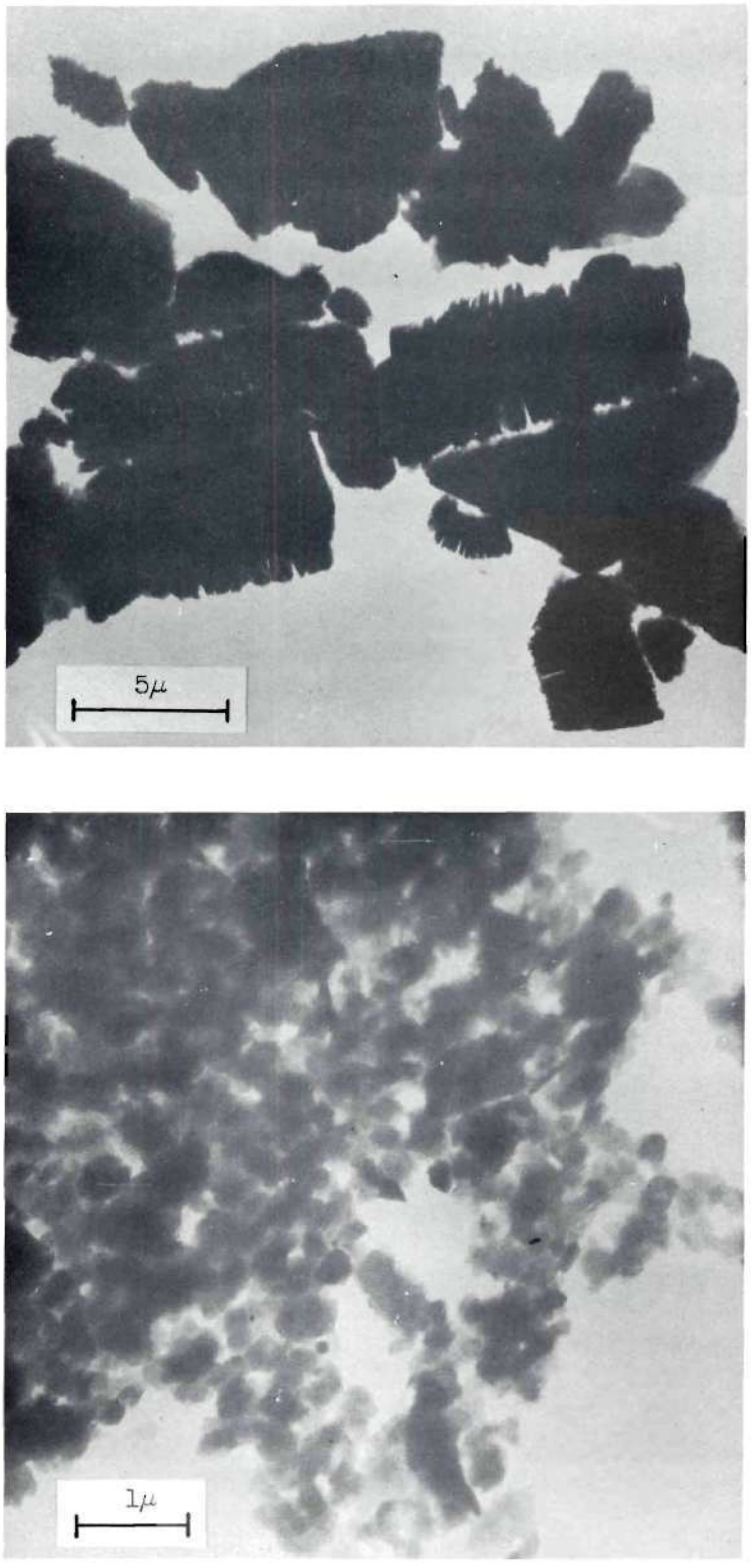

Figure 15. Electron Photomicrograph of ASTM Kaolin.

The reason for wide discrepancies in the values of the surface area of some of the samples as determined by stearic acid adsorption and the BET technique is not known. None of the materials studied was highly porous; therefore, it is hardly likely that the difference is due to parts of the surface being physically inaccessible to the long-chained molecules.

If the surface is accessible to the molecules, then it seems highly likely that lack of adsorption may be due to one of the following: (1) The gases normally present were not displaced by the solvent or were not completely removed by the degassing procedure for those samples so treated. (2) The surface was contaminated with some substance (other than gases) on which adsorption does not occur. (3) Certain crystal faces do not exhibit strong enough adsorptive forces for adsorption to occur.

While surface area values determined by stearic-acid adsorption are not as accurate as those determined by the BET procedure, this technique has the advantage of requiring less elaborate equipment and, for those cases where degassing is not required, of taking much less time.

The accuracy of surface area values obtained by the adsorption of stearic acid from solution can be ascertained only by comparison with some other standard (the BET values in this study). The technique should be of value, nevertheless, particularly in those cases where it is necessary to know only the relative value of the surface area of a powder compared to another powder of the same substance.

CHAPTER IV

CONCLUSIONS

(1) The values obtained for the surface area of solids as determined from measurement of the adsorption of stearic acid from solution were generally in good agreement with the results obtained by the BET method. Of the several methods used to determine the extent of adsorption, the use of the Langmuir trough is by far the most desirable from the viewpoint of time required, ease of manipulation, and accuracy.

(2) For the solids studied, degassing and vigorous heating of the sample are not necessary in most instances.

(3) Adsorption of stearic acid from solution seems to comply with the Langmuir adsorption theory, reaching a maximum value at low relative concentration.

(4) To determine the surface area of a solid it is usually necessary to make only one adsorption measurement if this measurement is made at relative concentration values of 0.3 or greater.

APPENDIX

APPENDIX I

DATA

TABLE II

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH CONDUCTOMETRIC TITRATION

Item No. from Table I	Sample Weight (g.)	Initial[a] Methanol Solution Concentration (g./l.)	Sodium Hydroxide Solution Normality	Aliquot (ml.)	Titration[b] End Point (ml. NaOH)	Specific Surface Area ($m^2/g.$)
5	0.1041	0.5976	0.00189	5	2.75	125.7
	0.0966	0.5034	0.00189	5	2.00	135.5
6	1.2901	0.5976	0.0189	25	1.00	12.9
	1.6060	0.5976	0.0189	25	0.39	13.9
7	0.8785	0.5976	0.0189	50	0.95	24.5
	0.8785	0.5976	0.0189	25	0.44	25.2
	0.7356	0.5976	0.0189	50	1.30	27.1
8	1.0346	0.5701	0.0189	50	1.13	18.9
	1.4781	0.5701	0.0189	50	1.07	13.4
9	1.2688	0.6703	0.0189	50	0.83	19.8
	1.5702	0.6703	0.0189	50	0.68	16.5
10	0.4826	0.6274	0.00946	20	3.37	16.1
11	0.7527	0.6274	0.00946	20	2.88	15.1
12	0.2591	0.6274	0.00946	20	4.70	6.2

(continued)

TABLE II (Continued)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH CONDUCTOMETRIC TITRATION

Item No. from Table I	Sample Weight (g.)	Initial[a] Methanol Solution Concentration (g./l.)	Sodium Hydroxide Solution Normality	Aliquot (ml.)	Titration[b] End Point (ml. NaOH)	Specific Surface Area ($m^2/g.$)
13	1.1876	0.6704	0.0189	50	1.50	16.9
14	0.4502	0.7166	0.0191	25	2.30	19.7
15	0.3837	0.5826	0.0191	25	0.70	48.7
16	0.2573	0.5826	0.0191	25	1.80	32.3
17	0.3553	0.5826	0.0191	25	2.06	16.8
18	1.3850	0.5034	0.00189	5	4.00	2.34
	1.9608	0.5034	0.00189	5	3.70	2.33
	1.3777	0.6141	0.0191	25	2.51	2.11
19	0.0791	0.6141	0.0191	25	1.42	166.8
	0.1118	0.6141	0.0191	25	0.67	181.2
	0.0575	0.6141[c]	0.0191	25	2.17	171.9
	0.0575	0.6141[c]	0.0191	25	2.07	196.6
20	25.0344	0.8407[d]	0.00189	5	8.80	0.64
	23.5792	0.8407[d]	0.00189	5	9.10	0.65
21	0.7767	0.5034	0.00189	5	4.10	3.57
	1.2510	0.5034	0.00189	5	3.90	2.98
22	30.4923	0.6141[e]	0.0191	25	2.54	0.11
23	30.2316	0.6141[d]	0.0191	25	2.27	0.09
24	33.0819	0.6478	0.0191	25	1.09	0.69
	32.0178	0.6478	0.0191	25	1.51	0.43

(continued)

TABLE II (Concluded)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH CONDUCTOMETRIC TITRATION

Item No. from Table I	Sample Weight (g.)	Initial[a] Methanol Solution Concentration (g./l.)	Sodium Hydroxide Solution Normality	Aliquot (ml.)	Titration[b] End Point (ml. NaOH)	Specific Surface Area ($m^2/g.$)
25	37.6376	0.4897[f]	0.00191	10	3.48	0.85
	37.6375	0.4897[f]	0.00191	10	3.26	0.88
	19.935	0.6478	0.0191	25	1.87	0.62
	10.0319	0.6141	0.0191	25	2.12	0.66
26	3.3694	0.5144[g]	0.0191	25	0.91	8.27
	0.9190	0.6274[d]	0.00946	25	2.08	8.17
	1.2143	0.6274[d]	0.00946	25	1.48	8.25
27	13.0601	0.6141	0.0191	25	2.50	0.23
28	12.5900	0.6141	0.0191	25	2.37	0.34
29	0.5429	0.51446	0.0191	25	0.98	24.5
	0.2448	0.6141	0.0191	25	2.19	24.2

a 100 ml. of stearic acid-methanol solution was used with each sample except as noted.
b Corrected for blank methanol consumption.
c 150 ml. of stearic acid-methanol solution was used.
d 50 ml. of stearic acid-methanol solution was used.
e 125 ml. of stearic acid-methanol solution was used.
f 250 ml. of stearic acid-methanol solution was used.
g 200 ml. of stearic acid-methanol solution was used.

TABLE III

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH THE HYDROPHIL BALANCE

Item No.	Sample Weight (g.)	Solvent	Initial Acid Concentration (g./l.)	Acid Solution Added to Sample (ml.)	Temper-ature (°F.)	Hydrophil Balance Reading for Sample (cm.)	Hydrophil Balance Reading for Blank (cm.)	Final Concentration (g./l.)	Surface Area of Sample* ($m^2/g.$)
1	10.6292	Benzene	4.2500	20	68	4.2	39.4	0.4530	3.1
	3.4266		4.2500	20	68	20.6	39.4	2.2208	5.1
	6.7314		8.5000	20	68	27.5	47.3	4.9417	4.6
	4.3193		17.0000	20	68	32.9	38.7	14.4497	5.1
	2.5956	Cyclo-	1.9455	20	68	14.6	39.2	0.7246	4.1
	8.5952	hexane	1.9455	20	68	30.0	39.2	1.4889	4.6
	2.1384		3.8910	20	68	29.8	42.2	2.7477	4.2
	2.2009		7.7821	20	68	34.7	40.3	6.7007	4.8
	10.2393		15.5643	20	68	26.0	38.9	10.4026	4.4
	4.5041		15.5643	20	68	33.4	38.9	13.3633	4.3
	1.1957	Methanol	0.6642	20	68	2.3	32.2	0.0474	4.5
	0.9333		0.6642	20	68	6.9	32.2	0.1423	4.8
	0.4743		0.6642	20	68	19.3	32.2	0.3981	4.9
	0.2830		0.6642	20	68	24.9	32.2	0.5139	4.6
	3.4661	Hexane	2.1912	20	68	6.4	42.6	0.3292	4.6
	1.4206		2.1912	20	68	26.6	42.6	1.3682	5.0
	3.3112		4.3823	20	68	24.4	42.6	2.5100	4.9
	5.7378		8.7647	20	68	24.4	40.7	5.2545	5.3
2	3.2831	Benzene	0.8500	20	68	13.6	36.8	0.6283	0.59
	5.4880		4.2500	20	68	34.3	39.5	3.6905	0.88

(continued)

TABLE III (Continued)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH THE HYDROPHIL BALANCE

Item No.	Sample Weight (g.)	Solvent	Initial Acid Concentration (g./l.)	Acid Solution Added to Sample (ml.)	Temperature (°F.)	Hydrophil Balance Reading for Sample (cm.)	Hydrophil Balance Reading for Blank (cm.)	Final Concentration (g./l.)	Surface Area of Sample* ($m^2/g.$)
2	8.6352	Benzene	14.4500	20	68	39.4	42.4	13.4275	1.0
	4.7679	Methanol	0.3321	20	68	1.5	36.8	0.0135	0.58
	0.2088		0.3321	20	68	14.9	36.8	0.1345	0.82
	4.6719		0.6642	20	68	15.8	32.2	0.3259	0.63
	1.7338		0.6642	20	68	24.2	32.2	0.4992	0.82
	10.1484	Cyclo-	1.9455	20	68	26.9	39.7	1.3182	0.62
	15.0033	hexane	5.8365	20	68	26.4	37.8	4.0759	1.02
	18.7978		9.7275	20	68	32.5	39.4	8.0239	0.79
	8.2440		15.5643	20	68	36.0	38.9	14.4036	1.21
	11.9618	Hexane	0.8765	20	68	16.0	34.3	0.4089	0.34
	9.4410		1.7530	20	68	27.3	36.5	1.3111	0.48
	4.0182		3.5060	20	68	34.9	38.3	3.1947	0.68
	13.8051		7.8885	20	68	32.8	35.8	7.2274	0.42
3	10.3006	Benzene	8.5000	20	68	9.8	47.3	1.7611	5.7**
	4.3907		8.5000	20	68	21.5	47.3	3.8664	9.2**
	7.5521		17.0000	20	68	18.7	38.7	8.2130	10 **
	1.2506		17.0000	20	68	35.4	38.7	15.5477	10 **
	4.8274		17.0000	20	68	26.8	38.7	11.7706	9.4**
	13.6320	Cyclo-	15.5643	20	68	4.6	42.3	1.6925	8.8**
	8.7149	hexane	15.5643	20	68	12.3	42.3	4.5258	11.0**

(continued)

TABLE III (Continued)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH THE HYDROPHIL BALANCE

Item No.	Sample Weight (g.)	Solvent	Initial Acid Concentration (g./l.)	Acid Solution Added to Sample (ml.)	Temperature (°F.)	Hydrophil Balance Reading for Sample (cm.)	Hydrophil Balance Reading for Blank (cm.)	Final Concentration (g./l.)	Surface Area of Sample* ($m^2/g.$)
3	4.5952	Cyclo-	15.5643	20	68	24.3	42.3	8.9412	12.5**
	2.7312	hexane	15.5643	20	68	33.9	42.3	12.4735	9.8**
	0.9305		15.5643	20	68	39.3	42.3	14.4604	10.2**
	0.8846	Methanol	0.6642	20	68	1.5	32.2	0.0309	6.2**
	0.5152		0.6642	20	68	4.2	32.2	0.0866	9.7**
	0.3623		0.6642	20	68	10.3	32.2	0.2125	10.8**
	0.2636		0.6642	20	68	16.9	32.2	0.3486	10.4**
	0.1322		0.6642	20	68	24.0	32.2	0.4951	11.1**
	6.6766	Hexane	8.7647	20	68	4.0	39.6	0.8853	10.1**
	5.2777		8.7647	20	68	9.9	39.6	2.1912	10.8**
	4.7650		8.7647	20	68	13.6	39.6	3.0101	10.5**
	3.0771		8.7647	20	68	21.8	39.6	4.8250	11.1**
	0.9941		8.7647	20	68	33.9	39.6	7.5031	11.0**
4	7.2853	Benzene	4.2500	20	68	6.4	39.5	0.6886	4.2
	3.3646		8.5000	20	68	29.6	47.3	5.3136	8.2
	8.4253		17.0000	20	68	20.2	38.7	8.8718	8.4
	3.3632		17.0000	20	68	19.8	38.7	8.6962	8.3
	16.3946	Cyclo-	15.5643	20	68	3.4	42.3	1.2510	8.1
	12.6381	hexane	15.5643	20	68	8.2	42.3	3.0172	8.6
	8.9673		15.5643	20	68	17.6	42.3	6.4758	8.8

(continued)

TABLE III (Continued)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH THE HYDROPHIL BALANCE

Item No.	Sample Weight (g.)	Solvent	Initial Acid Concentration (g./l.)	Acid Solution Added to Sample (ml.)	Temperature (°F.)	Hydrophil Balance Reading for Sample (cm.)	Hydrophil Balance Reading for Blank (cm.)	Final Concentration (g./l.)	Surface Area of Sample* ($m^2/g.$)
4	6.3201	Cyclo-	15.5643	20	68	26.0	42.3	9.5667	8.2
	1.8772	hexane	15.5643	20	68	37.3	42.3	13.7245	8.4
	0.6605	Methanol	0.6642	20	68	3.5	32.2	0.0722	7.8
	0.5847		0.6642	20	68	5.4	32.2	0.1114	8.2
	0.5502		0.6642	20	68	6.4	32.2	0.1320	8.4
	0.6460		0.6642	20	68	6.9	32.2	0.1423	7.0
	0.4439	Methanol	0.6642	20	68	12.3	32.2	0.2537	8.0
	0.1150		0.6642	20	68	26.9	32.2	0.5549	8.2
	9.0247	Hexane	8.7647	20	68	4.9	39.6	1.0845	7.4
	6.5950		8.7647	20	68	10.3	39.6	2.2797	8.5
	5.0566		8.7647	20	68	17.2	39.6	3.8069	8.1
	2.1341		8.7647	20	68	30.1	39.6	6.6621	8.2
30	1.0373	n-Propanol	10.0020	10	85	36.7	44.8	8.1941	7.6
31	3.0488	n-Propanol	10.0020	10	85	36.7	43.8	8.3810	2.6
32	3.0421	n-Propanol	10.0020	10	85	29.2	44.8	6.5191	5.0
33	0.7274	Benzene	16.7235	5	68	19.7	38.7	8.6470	24.1
34	1.6081	Benzene	16.7235	10	68	25.0	38.1	10.8032	16.1
35	2.3251	Methanol	0.6214	100	68	32.5	48.1	0.4199	3.6
	1.8592		0.6214	100	68	35.0	48.1	0.4522	3.8**
	1.0339	Benzene	2.3827	10	49	27.7	37.6	1.7350	2.6

(continued)

TABLE III (Concluded)

EXPERIMENTAL DATA FOR STEARIC ACID ADSORPTION
CONCENTRATIONS MEASURED WITH THE HYDROPHIL BALANCE

Item No.	Sample Weight (g.)	Solvent	Initial Acid Concentration (g./l.)	Acid Solution Added to Sample (ml.)	Temperature (°F.)	Hydrophil Balance Reading for Sample (cm.)	Hydrophil Balance Reading for Blank (cm.)	Final Concentration (g./l.)	Surface Area of Sample* ($m^2/g.$)
35	0.2847	Benzene	2.3827	10	49	34.0	37.6	2.1451	3.5**
	1.7926		2.3827	10	49	28.6	42.3	1.6109	3.7**
36	0.2937	Benzene	2.3827	10	51	26.8	30.1	2.1215	3.8
	0.7724		2.3827	10	51	19.8	30.1	1.5673	4.6
	1.1190		2.3827	10	51	12.8	30.1	1.0132	5.3
37	1.9373	Benzene	2.3827	25	50	39.8	43.7	2.1700	1.2
	1.5917		2.3827	10	52	30.0	42.4	1.6853	1.8**
	1.1396		2.3827	10	50	38.0	44.0	2.0578	1.2
38	6.8323	Benzene	9.4672	10	68	44.8	46.0	9.2202	0.13
	6.7033		6.6371	10	68	43.5	44.8	6.4445	0.14
	4.3417		4.9922	10	60	32.2	33.0	4.8711	0.12
	7.2506		4.9922	10	60	31.5	33.0	4.7653	0.14
39	0.5134	Benzene	9.4672	10	68	41.6	43.4	9.0740	3.4
	0.3298		9.4672	10	68	42.0	43.4	9.1836	3.7
40	3.9184	Benzene	1.3233	10	50	29.2	38.4	1.0070	0.22

* Unless otherwise indicated, sample preparation consisted of drying in a vacuum oven at a temperature of 110° C. and an absolute pressure of 1 inch Hg. or less for at least two hours.

** Sample preparation consisted of heating to 110° C. at a pressure of 0.1 micron or lower for one hour or more.

TABLE IV

THE SOLUBILITY OF STEARIC ACID IN VARIOUS SOLVENTS*

Solvent	Grams acid per 100 g. solvent					
	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.
Benzene	0.24	2.46	12.4	51.0	145	468
Cyclohexane	0.2	2.4	10.5	43.8	133	450
Methanol	---	0.1	1.8	11.7	78	520

*Data of A. W. Ralston and C. W. Hoerr as reported by K. S. Markley (22).

SOLVENT PURIFICATION

The benzene used was Baker's reagent grade. This was dried by immersing in the benzene considerable quantities of freshly cut sodium particles. Every few days additional freshly cut sodium was added. After three weeks the benzene was refluxed over fresh sodium for three hours; it was then transferred, without contact with the atmosphere, into a distilling flask of a closed-distillation system. The benzene was distilled over sodium through a three-foot column packed with quarter-inch Raschig rings, the first twenty-five per cent being discarded due to the possibility of moisture pick-up from the distillation system, and the fraction boiling between 79.4° and 79.5° C. being retained for adsorption measurements. The benzene had a refractive index of 1.4976 at 25° C.

Phillips's research-grade normal hexane was purified by refluxing over freshly cut sodium for two hours, distilled from over sodium, then fractionated three times through the same column used for the benzene. The middle fifty per cent was retained in each fractionation. The boiling range of the final product was 68.6° to 68.7° C. with a refractive index of 1.3720 at 25° C.

Reagent-grade methanol was purified by storing for a week over calcium oxide which had been heated to 850° C. The alcohol was then refluxed over fresh calcium oxide for six hours. It was then distilled and fractionated three times. The boiling range of the product was 64.2° to 64.3° C. with a refractive index of 1.3267 at 25° C.

Eastman's white-label cyclohexane was purified by the same

procedure used for the normal hexane. The boiling range of the final product was 80.6° to 80.7° C. with a refractive index of 1.4235 at 25° C.

After purification the solvents were either used immediately to make up stock solutions of stearic acid solution or stored in bottles fitted with a glass delivery tube and a drying tube containing calcium chloride. In either event, if more than three days had elapsed since the solvent was purified, fresh solvent was prepared.

The methanol used in the conductivity cell was distilled from over calcium oxide and no further purification used. The boiling range of this product was 64.0° to 64.6° C.

APPENDIX III

NOMENCLATURE

C	concentration
C_o	saturation concentration
m	mass of adsorbent
n	number of molecules striking surface every second
N	Avogadro's number
P	pressure
P_o	saturation pressure
R	gas constant
T	temperature
v	volume of gas adsorbed at pressure, P
v_m	volume of gas adsorbed when the surface is completely covered with a unimolecular layer
x	grams adsorbed
γ	interfacial tension
Γ_2	surface excess of solute
θ	fraction of surface covered
μ	chemical potential
μ^o	chemical potential in standard state

(continued)

APPENDIX III (Concluded)

σ number of adsorbed molecules per unit area of surface

σ_o number of adsorbed molecules in one complete layer per unit area of surface

τ average length of time that a molecule remains on the surface

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VITA

Preston Talmage Bankston was born in Pascagoula, Mississippi, on March 31, 1924. He received his elementary and high school education in Tarrant, Alabama, graduating in June, 1942. In October, 1942, he entered the United States Navy as an aviation cadet and was commissioned Ensign in June, 1944. After advanced operational flight training, he served overseas in the Central Pacific Theater in 1945 and 1946, being released from active duty in 1946.

After attending Northeastern University, Boston, Massachusetts, for a year, in 1947-1948, Mr. Bankston entered Georgia Institute of Technology in September, 1948, receiving a Bachelor of Chemical Engineering degree in December, 1950. He entered the Graduate School of Georgia Institute of Technology in January, 1951, to work toward a Doctor of Philosophy degree in Chemical Engineering.

Mr. Bankston is a member of the Georgia Academy of Science and the American Chemical Society, and a Junior Member of the American Institute of Chemical Engineers.